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THE UNIVERSITY OF ALBERTA

- A. OBSERVATIONS RELATED TO THE PREPARATION OF
9,10-EPOXY-9,10-DIPHENYL-9,10-DIHYDROANTHRACENE.
- B. THE UTILITY OF ORGANOBORANES IN ORGANIC SYNTHESIS.
A NOVEL SYNTHESIS OF ALDEHYDES.

by



GEOFFREY F. MORRISON

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES IN PARTIAL
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of

MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

FALL, 1969

UNIVERSITY OF ALBERTA
FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read,
and recommend to the Faculty of Graduate Studies
for acceptance, a thesis entitled

- A. OBSERVATIONS RELATED TO THE PREPARATION OF
9,10-EPOXY-9,10-DIPHENYL-9,10-DIHYDROANTHRA-
CENE.
- B. THE UTILITY OF ORGANOBORANES IN ORGANIC
SYNTHESIS. A NOVEL SYNTHESIS OF ALDEHYDES .

submitted by Geoffrey F. Morrison, in partial
fulfilment of the requirements for the degree
of Master of Science.



To Pat.

A C K N O W L E D G E M E N T S

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A B S T R A C T

The conditions reported to oxidise 2-iodobenzoic acid to the iodoso derivative were found to result in concomitant nitration, giving predominantly 5-nitro-2-iodosobenzoic acid. Transformation of the latter to the 2-aryliodonobenzoate produced a novel "4-nitro-benzyne" precursor.

9,10-Epoxy-9,10-diphenyl-9,10-dihydroanthracene was prepared and found to be more stable thermally than had been reported.

Trihexylborane was observed to react with the terminal nitrogen of diethyl diazomalonate to yield a N-substituted hydrazone.

A novel ethanalation was achieved by reaction of trialkylboranes with diazoacetaldehyde to give aldehydes in good yield.

However, two boronic acid esters did not react with ethyl diazoacetate and the reaction of a trialkylborane with an acyl azide was also unsuccessful.

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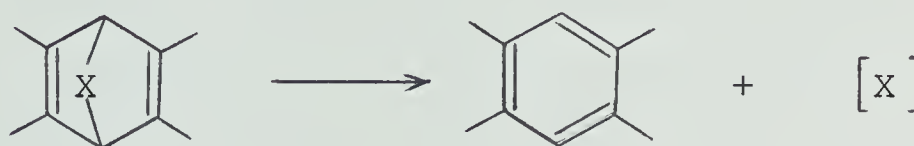
I. A Comparison of Properties Reported⁶ for 2-Phenyliodonobenzoate (9) with Properties Observed for the Products Prepared by the Procedures of Beringer and Huang⁶, and Fieser and Haddadin.¹⁴ 7

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OBSERVATIONS RELATED TO THE PREPARATION OF 9,10-EPOXY-
9,10-DIPHENYL-9,10-DIHYDROANTHRACENE

I N T R O D U C T I O N

A number of endo-bridged polycyclic compounds are known to undergo thermally induced elimination of the bridging moiety with concomitant formation of an aromatic system.



If the extrusion is carried out in the presence of a suitable acceptor agent to trap [X] this may constitute a useful synthetic method.

Wasserman and Scheffer¹ have thus used the thermal decomposition of 9,10-peroxy-9,10-diphenyl-9,10-dihydroanthracene to bring about typical singlet oxygen reactions.

The stereospecific cis-hydrogenation of multiple bonds has been achieved by Corey and Mock², by warming the substrate with anthracene-9,10-biimine. These authors have presented evidence that the active reducing species is the extrusion fragment, diimide.

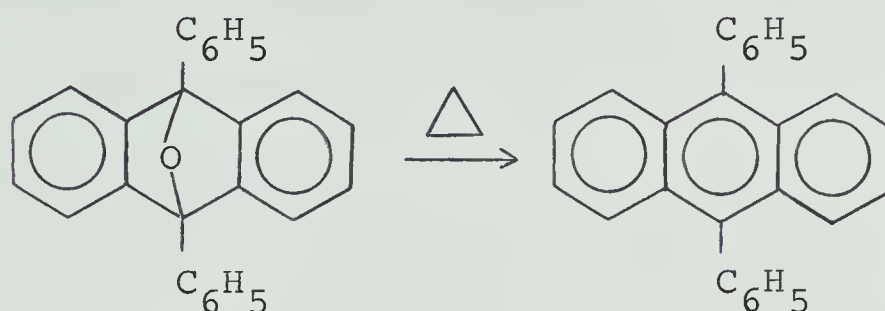
The extrusion moiety dimethyl silylene has been trapped with diphenylacetylene to produce 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disilacyclohexadiene. This extrusion was accomplished by Gilman and co-workers³ by pyrolysis of

1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene.

Similarly, Peddle et al ⁴ have reported evidence for the formation of tetramethyldisilene by extrusion from suitably bridged dihydroaromatic systems.

The loss of an atomic oxygen bridge was noted by Seyferth and Menzel ⁵ during the attempted purification of 5,8-epoxy-1,2,3,4-tetraphenyl-5,8-dihydronaphthalene by chromatography over neutral alumina.

A similar loss has been reported by Beringer and Huang ⁶ on heating 9,10-epoxy-9,10-diphenyl-9,10-dihydroanthracene in diglyme at 162° for 2 hours.

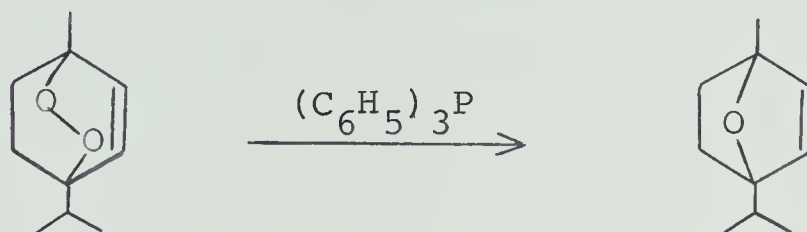


The fate of the oxygen atom was not reported by these authors and was the subject of the present investigation. Thus it was hoped that the thermolysis of 9,10-epoxy-9,10-diphenyl-9,10-dihydroanthracene in the presence of a suitable acceptor might produce a novel oxidation reaction. With this notion in mind the preparation and investigation of the thermal behaviour of 9,10-epoxy-9,10-diphenyl-9,10-dihydroanthracene was instigated.

During the course of this work a novel method of generation of 4-nitrobenzyne was discovered. The formation of this benzyne in the presence of three known

trapping agents afforded the corresponding nitro-substituted adducts.

The reduction of a 1,4-peroxy bridge to the epoxy derivative had been achieved by Horner and Jurgeleit ⁷, for the conversion of ascaridole to 1,4-cineole, by using triphenylphosphine as the reductant.

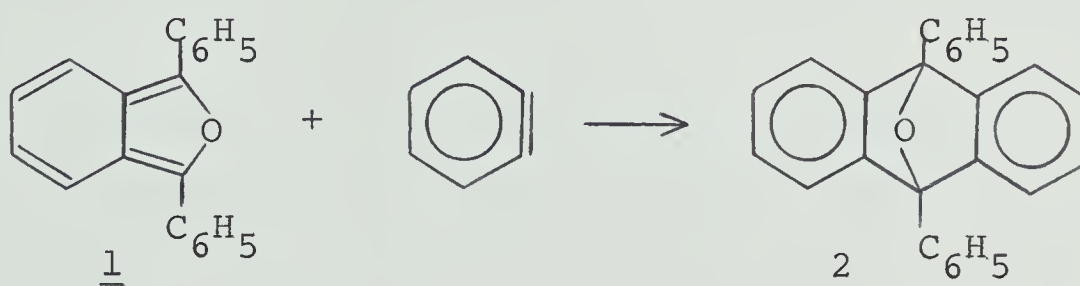


Consequently a brief investigation of the possible synthesis of 9,10-epoxy-9,10-diphenyl-9,10-dihydroanthracene from the peroxy analog, by the action of triphenylphosphine, was also conducted.

R E S U L T S A N D D I S C U S S I O N

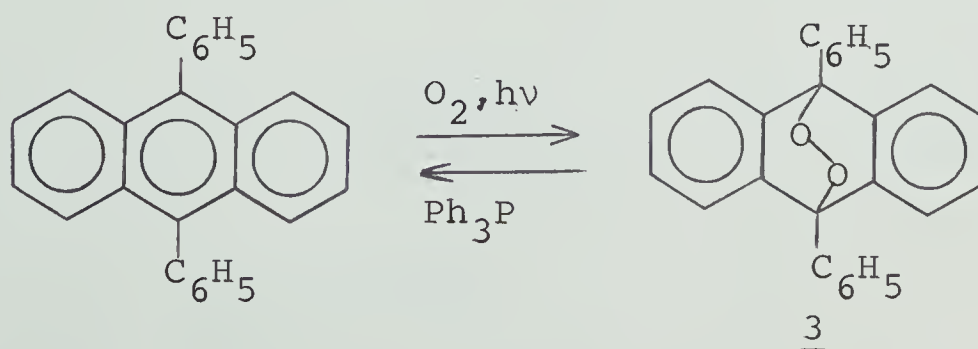
The initial objective of the present study was the synthesis of 9,10-epoxy-9,10-diphenyl-9,10-dihydroanthracene (2) in order to investigate its thermal behaviour.

The synthesis of 2 had twice been reported in the literature ^{6,8} and both of these methods involved the Diels-Alder type addition of benzyne across the diene system of 1,3-diphenylisobenzofuran (1).



Initially an alternative approach to 2 was briefly investigated. Horner and Jurgeleit ⁷ had reduced the naturally occurring peroxide, ascaridole, to the epoxy derivative, 1,4-cineole, by heating with triphenylphosphine in petroleum ether for 65 hours.

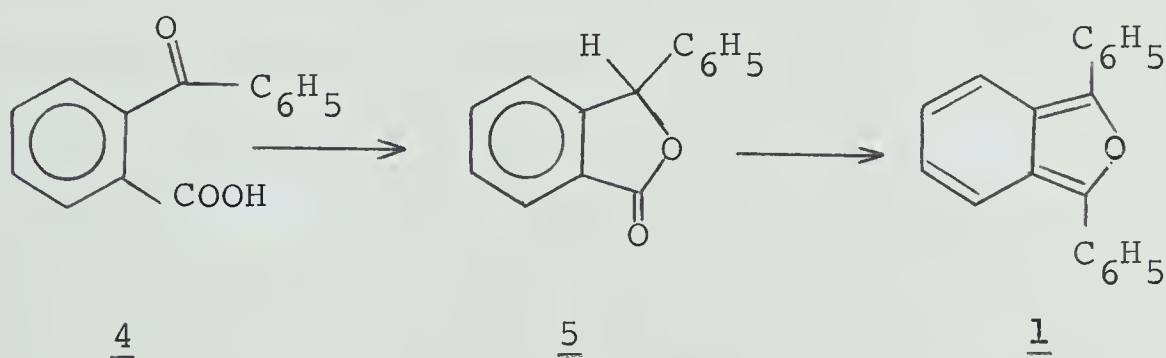
The corresponding peroxide, 9,10-peroxy-9,10-diphenyl-9,10-dihydroanthracene (3), was readily available from the photosensitised autoxidation of 9,10-diphenylanthracene. ⁹



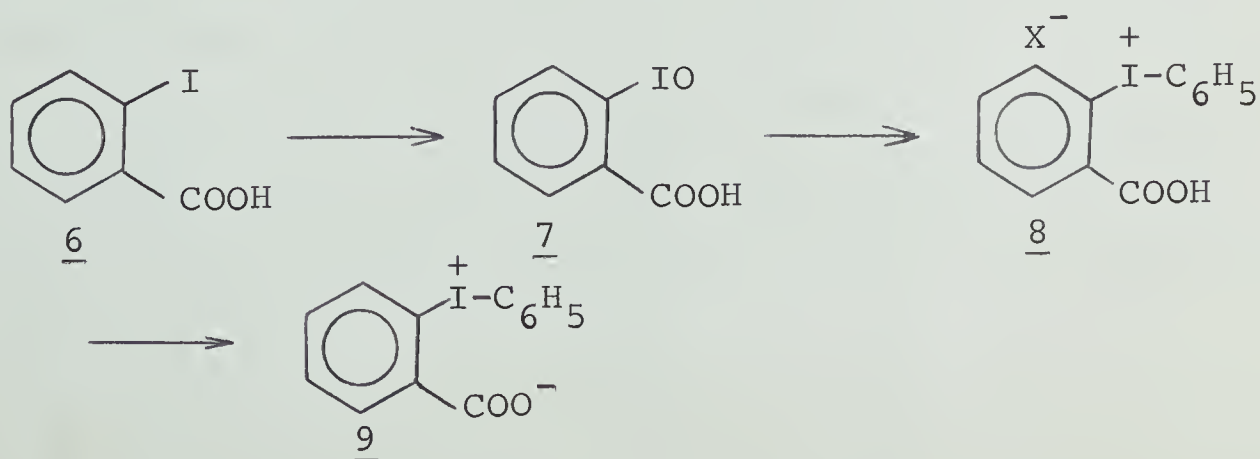
Due to the low solubility of the transannular peroxide in petroleum ether, toluene was employed as the reaction solvent. However, after heating the reaction mixture for 65 hours on a steam bath only triphenylphosphine oxide and 9,10-diphenylanthracene could be detected by tlc.

The synthesis of 2 reported by Beringer and Huang ⁶ was then attempted, wherein the benzyne is generated by the thermolysis of the betaine, 2-phenyliodonobenzoate (9).

The diene (1) was prepared from 2-benzoylbenzoic acid (4) by reduction with zinc dust in acetic acid to the lactone 3-phenylphthalide ¹⁰ (5), which was then reacted with phenylmagnesium bromide to yield 1. ¹¹



The detailed procedure for the synthesis of 9, as described by Beringer and Huang ⁶, was followed.



Thus, treatment of 2-iodobenzoic acid (6) with a fuming nitric-concentrated sulfuric acid mixture at 100° for one hour yielded a colorless solid, mp 195-198° (lit ⁶ 2-iodosobenzoic acid (7) 200°). Acid-catalysed condensation of this product with benzene and treatment of the resultant iodonium salts with aqueous sodium hydroxide yielded the inner salt. Recrystallisation from chloroform:methanol afforded colorless crystals, mp 220-221° dec (lit ⁶ 2-phenyliodonobenzoate (9) 205° dec, monohydrate 220° dec). The ultraviolet and infrared spectra were in excellent agreement with the spectral data reported.⁶ The nmr spectrum was in reasonable agreement in view of the fact that the solvent used had not been reported by these authors (Table I).

Although the melting point was not in agreement with that reported for the unhydrated salt (the expected product), it was felt that this was explicable in view of the range of melting points for 9 which have been reported, viz ¹² 229-230° (analysis fits for unhydrated salt), ¹³ 220.5 - 221°, ¹⁴ 219-220° dec, ¹⁴ 220-222° dec (monohydrate), ¹⁴ 215-216° dec (unhydrated).

Also, since the spectral data were consistent the material was used for the next stage in the sequence.

The betaine salt was reacted with 1 as described ⁶ to afford a yellow solid. Recrystallisation gave very pale yellow crystals, mp 189-190° (lit ^{6,8} 2 188-188.5°).

TABLE I

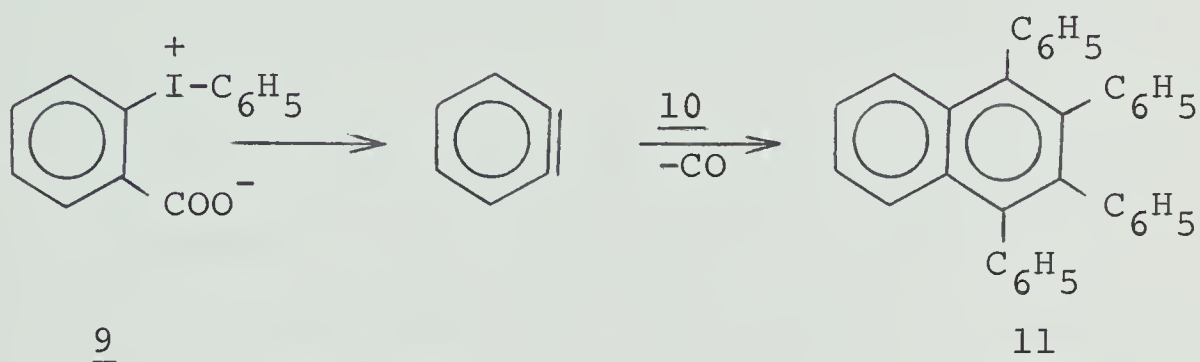
A Comparison of Properties Reported ⁶ for 2-Phenylidoniobenzoate (9) with Properties Observed for the Products Prepared by the Procedures of Beringer and Huang, ⁶ and Fieser and Haddadin.¹⁴

| Property | Reported ⁶ | Observed ⁶ | Observed ¹⁴ |
|------------------------------|-------------------------------|-------------------------------|-------------------------------|
| Melting Point | 205° dec (unhydrated) | 220-221° dec | 226-227° dec |
| | 220° dec (monohydrate) | | |
| uv max (H ₂ O) mμ | | | |
| (log ε) | 205(4.43) , 266(4.02) | 205(4.24) , 266(4.02) | 207(4.38) , 226(sh) |
| ir(KBr) cm ⁻¹ | 3005(w) , 1630(s) , 1524(s) , | 3100(w) , 3050(w) , 1625(s) , | 3080(w) , 3050(w) , 1610(s) , |
| (Intensity) | 1400(m) , 1335(s) , 1005(w) , | 1522(s) , 1400(m) , 1342(s) , | 1553(w) , 1437(m) , 1347(s) , |
| | 995(w) , 817(m) , 738(s) , | 1338(s) , 1005(m) , 990(m) , | 989(m) , 825(m) , 744(s) , |
| | 720(s) , 685(m) . | 817(m) , 735(s) , 721(s) , | 683(m) . |
| | | 685(m) . | |
| nmr (DMSO-d ₆) τ | Fine structure between | Fine structure between | Fine structure between |
| | 1.46 - 3.28* | 1.34 - 3.06 | 1.86 - 3.32 |

* solvent was not reported

However, the mass spectrum showed a parent ion at $\underline{m/e}$ 391 (Calcd for $C_{26}H_{18}O$ $[M]^+$ 346) and compositional analyses for carbon and hydrogen were some 10% and 1% lower, respectively, than expected.

It was therefore decided to check the authenticity of the betaine salt by reaction with 2,3,4,5-tetraphenylcyclopentadienone (10), a reaction which is well documented.¹⁴



The product was a yellow solid, mp 275 - 277°, obtained in 86% yield, whereas the expected 1,2,3,4-tetraphenylphenanthrene (11) is a colorless solid, mp 203 - 204°. ¹⁴ The mass spectrum of the product showed a molecular ion at $\underline{m/e}$ 477 (Calcd for $C_{34}H_{24}$; 432).

An alternative mode of preparation of 9 due to LeGoff¹³ and modified by Fieser and Haddadin¹⁴, was then employed. The oxidation of 2-iodobenzoic acid was achieved by potassium persulfate and the betaine obtained exhibited marked differences in spectral properties from those reported by Beringer and Huang⁶ (see Table I). This latter product was decomposed in the presence of 10 and 1 respectively, and the products isolated, exhibited

physical properties, spectral data and elemental analyses consistent with their formulation as 11 and 2 respectively. The latter product was reduced to 9,10-diphenylanthracene with zinc dust in acetic acid.⁸

At this time a comparison was made of the infrared spectra of the betaine obtained using $\text{HNO}_3 - \text{H}_2\text{SO}_4$ as the oxidant, and the two adducts obtained from decomposition of this salt, with the corresponding spectra of the betaine obtained using $\text{K}_2\text{S}_2\text{O}_8$ as the oxidant, and the adducts obtained therefrom.

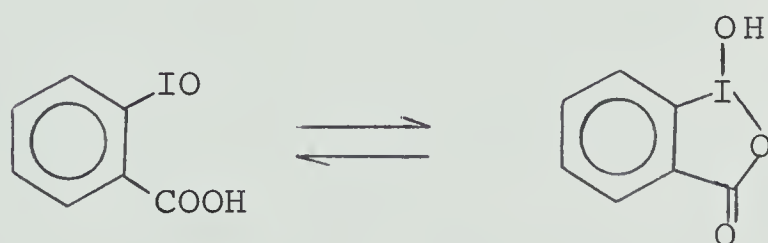
The former three compounds exhibited a pair of strong absorption bands at ca 1520 and ca 1340 cm^{-1} , which were notably absent from the spectra of the latter group. These bands are characteristic of the symmetric and asymmetric stretching frequencies of the nitro function.¹⁵

Thus it became apparent that the conditions ($\text{HNO}_3 - \text{H}_2\text{SO}_4$) employed for the oxidation ($\text{ArI} \rightarrow \text{ArIO}$) were also adequate to effect aromatic electrophilic substitution producing a nitro-substituted iodosobenzoic acid, and subsequently a nitro-substituted 2-phenyliodonobenzoate. Thermolysis of the latter presumably generated a nitro-benzyne, and the adducts formed by trapping this benzyne were therefore also nitro-substituted. The elemental analyses and spectral data were consistent with nitro-substituted derivatives for the former series.

The prescribed oxidation⁶ of 2-iodobenzoic acid

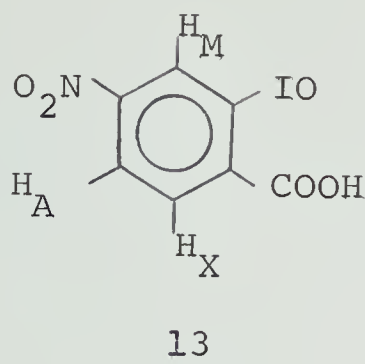
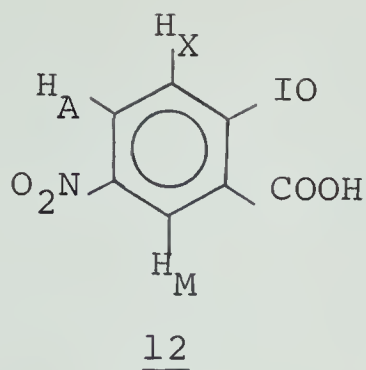
using $\text{HNO}_3 - \text{H}_2\text{SO}_4$ was then repeated in order to investigate the product(s) formed. Fractional crystallisation from water of the crude oxidation reaction mixture afforded two compounds in 54% and 15% yields.

The major component was identified as 5-nitro-2-iodosobenzoic acid (12). The molecular formula was determined as $\text{C}_7\text{H}_4\text{NIO}_5$ from the elemental analysis. The infrared spectrum showed strong absorptions at 1523 and 1348 cm^{-1} characteristic of a nitro group. A further strong band at 1616 cm^{-1} was attributed to the carbonyl of an ortho-iodosobenzoic acid. (The exceptionally low value for the frequency of this functionality is thought to be due to the formation of an intramolecularly bonded species.¹⁶).



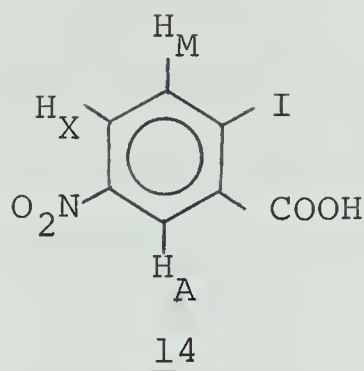
The nmr spectrum showed an AMX system with absorptions centred at τ 1.24, 1.38 and 1.85 with $J_{\text{AM}} = 2.5\text{ Hz}$, $J_{\text{AX}} = 9\text{ Hz}$ and $J_{\text{MX}} = 0.5\text{ Hz}$ for the aromatic protons, but no signal was observed for the carboxylic acid proton.

This combination of one ortho, one meta and one para coupling constant indicates a 1,2,4(5)-trisubstituted benzene (12 or 13).



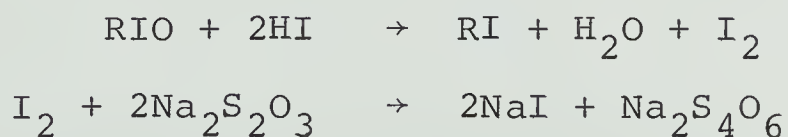
Goldstein and Grampoloff ¹⁷ had reported the isolation of 5-nitro-2-iodobenzoic acid (12) in about 50% yield from reaction of 2-iodobenzoic acid with a fuming nitric-concentrated sulfuric acid mixture at 135° for one hour. They reduced 12 to the iodo derivative by treatment with acidified potassium iodide and showed that the product was identical to that obtained by diazotisation of 5-nitroanthranilic acid, followed by treatment with potassium iodide.

A similar reduction of the product from the present investigation yielded 5-nitro-2-iodobenzoic acid (14) mp 194 - 197° (lit ¹⁷ 14 194°, ¹⁸ 197 - 198°, 4-nitro-2-iodobenzoic acid ¹⁹ 143°). The infrared spectrum of 14 exhibited absorption at 1710 cm⁻¹ (C=O of COOH) as well as bands at 1525 and 1345 cm⁻¹ (NO₂). The nmr spectrum showed a well-defined AMX system for the aromatic protons with signals centred at τ 1.56, 1.68 and 1.98 with $J_{AM} \sim 0.4$ Hz, $J_{MX} = 8.7$ Hz and $J_{AX} = 2.7$ Hz. This shows the marked effect on the chemical shift of the H-4 proton caused by reduction of the iodoso group (12 \rightarrow 14), as well as lesser effects on the H-3 and H-6 protons.



An attempt was made to obtain the molecular weight of 12 by mass spectroscopy but an extremely facile loss of an oxygen atom prevented the appearance of the molecular ion (m/e 309), although the [M - 16] peak (m/e 293) was observed to be the base peak.

An indirect method of obtaining the molecular weight was therefore employed utilising the oxidising ability of the iodoso group. This technique, due to Twiss and Heinzelmann ²⁰, is dependent upon the quantitative oxidation of acidified potassium iodide by the iodoso compound, followed by titration of the liberated iodine with sodium thiosulfate solution.



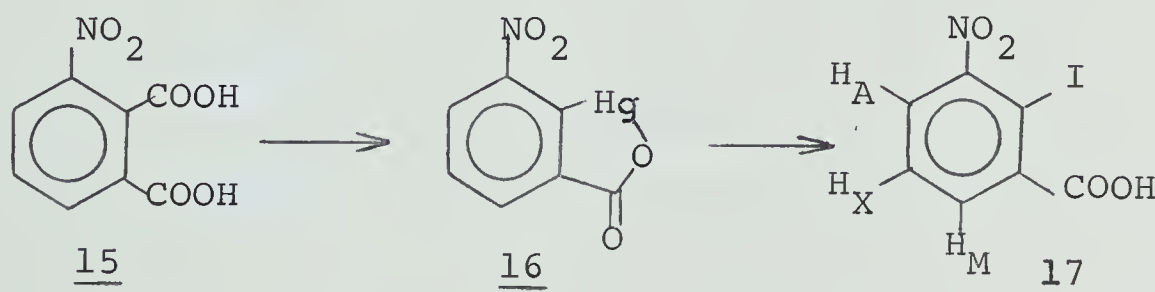
The molecular weight was determined as 311.6 (Calcd for $\text{C}_7\text{H}_4\text{NIO}_5$: 309).

The minor product was assigned the formulation 3-nitro-2-iodobenzoic acid [17) on the basis of spectral data and the elemental analysis, which was consistent with $\text{C}_7\text{H}_4\text{NIO}_4$. The infrared spectrum showed absorption

at 1710 cm^{-1} (COOH) and absorptions at 1540 and 1374 cm^{-1} (NO_2). The nmr spectrum exhibited an AMX system with signals at τ 2.09, 2.19 and 2.35 with $J_{\text{AM}} = 2\text{ Hz}$, $J_{\text{AX}} = 7\text{ Hz}$ and $J_{\text{MX}} = 8\text{ Hz}$, indicative of a 1,2,3-trisubstituted benzene. No signal for the carboxylic acid proton could be observed.

The minor product was recovered unchanged when treated with acidified potassium iodide, indicating the absence of an iodoso function.

Confirmation of the assignment as the 3-nitro derivative was provided by the independent synthesis of 17 from 3-nitrophthalic acid (15) via anhydro-2-hydroxymercuri-3-nitrobenzoic acid (16) by the method of Whitmore and Culhane.^{21,22}



The infrared and nmr spectra of the two products were identical.

The 5-nitro-2-iodosobenzoic acid was condensed with benzene in concentrated sulfuric acid and the iodonium salts obtained were reacted with aqueous sodium hydroxide solution to afford 5-nitro-2-phenyliodonobenzoate (18).

This betaine salt was shown to be spectroscopically

identical to the inner salt obtained using the method of Beringer and Huang ⁶ (vide supra).

Hence it was confirmed that using the conditions described by Beringer and Huang for the oxidation of 2-iodobenzoic acid resulted in the concomitant nitration of the benzene ring.

The infrared absorption bands at 1524 and 1335 cm^{-1} and the uv maximum at 266 m μ reported by these authors for the betaine would seem to indicate a nitro-substituted product, although this evidence is incompatible with the elemental analysis which is reported.

However the use of this method in the present work had unwittingly led to the observation of a novel synthetic route to 4-nitrobenzyne. As a further illustration of the synthetic utility of 18 as a nitrobenzyne precursor, the betaine was decomposed in the presence of anthracene (23). 2-Nitrotriptycene (22) was obtained in 43% yield.

The nmr spectrum showed a doublet centered at τ 1.80 with $J = 2.5$ Hz, and a doublet of doublets at τ 2.08 with $J = 2.5$ and 8.5 Hz. These two signals at low field are typical of protons ortho to a nitro function. The combination of one meta and one meta plus one ortho coupling constant confirmed that the nitro group was substituted at the β -position.

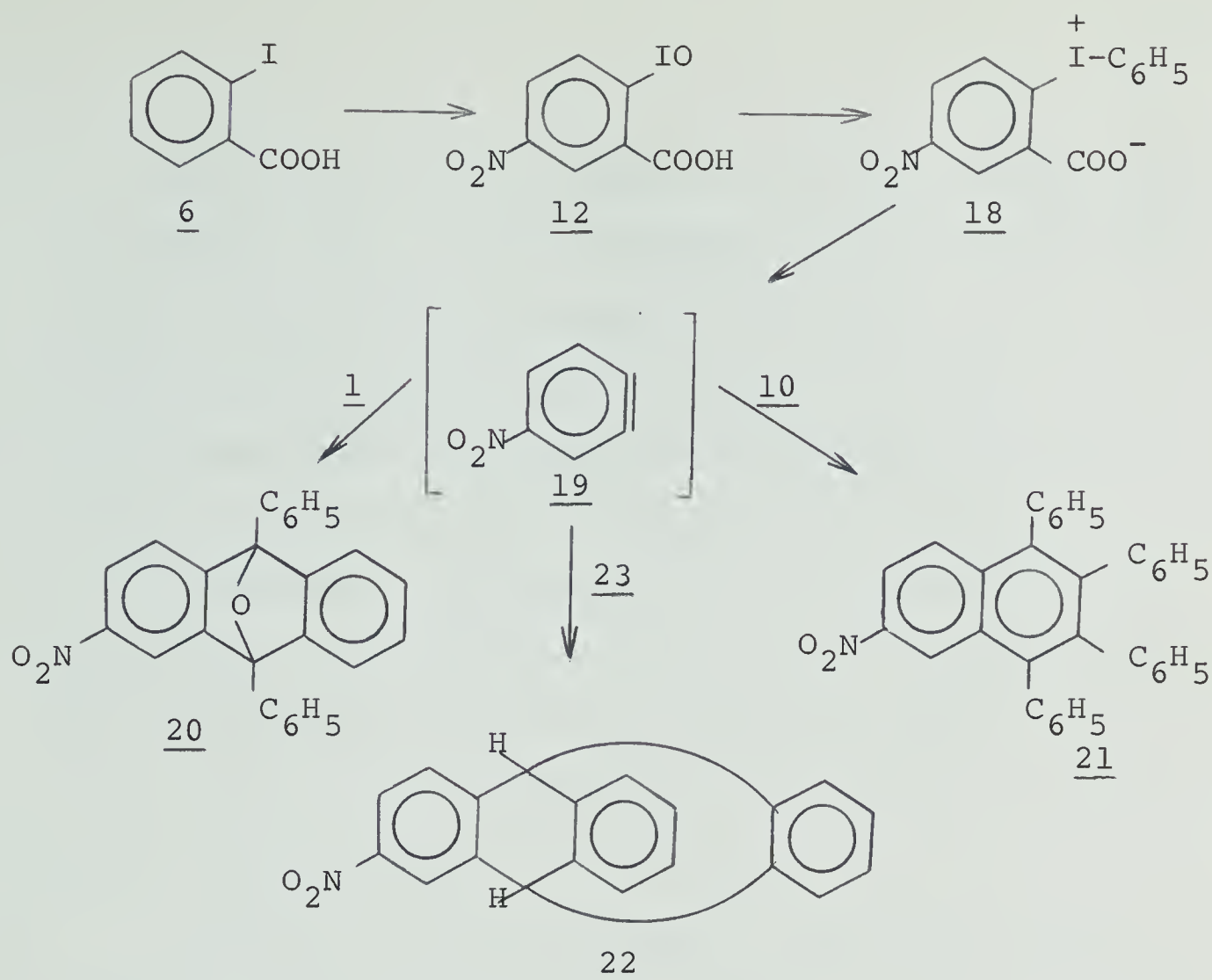
Nmr spectroscopy was also used to demonstrate that the nitro group in the two adducts obtained by trapping

the presumed nitrobenzyne intermediate with 10 and 1 was also substituted at the β -position.

The product with 10 was shown to be 6-nitro-1,2,3,4-tetraphenylnaphthalene (21). A doublet of doublets centered at τ 1.35 with $J = 0.5$ and 2.5 Hz showing a para and meta coupling was assigned to H-5. A further doublet of doublets centered at τ 1.87 with $J = 2.5$ and 8.5 Hz was assigned to the H-7 proton by virtue of the meta and ortho couplings. Again these signals at low field are typical of protons ortho to the nitro group. The third naphthalene proton, H-8, was present as a doublet of doublets centered at τ 2.22 with $J = 0.5$ and 8.5 Hz.

The product of reaction of the nitrobenzyne with 1 was shown to be 2-nitro-9,10-epoxy-9,10-diphenyl-9,10-dihydroanthracene (20). Although the nmr spectrum was complex, a discrete doublet at τ 1.94 with $J = 2.5$ Hz indicated that the proton ortho to the nitro group had a meta (and probably a para) coupling. This can only be explained by a β -nitro group.

In summation, treatment of 2-iodobenzoic acid (6) with $\text{HNO}_3 - \text{H}_2\text{SO}_4$ at 100° for one hour produced predominantly 5-nitro-2-iodosobenzoic acid (12), which was exclusively transformed into 5-nitro-2-phenyliodonio-benzoate (18). Thermolysis of 18 generated 4-nitrobenzyne (19), which was trapped by 1 to give 20, by 10 to give 21, and by 23 to give 22.



The formation of 4-nitrobenzyne by this route compares favorably with the procedure of Paget and Burger ²³, who generated 4-nitrobenzyne by diazotisation of 4-nitroanthranilic acid and in the presence of anthracene obtained 2-nitrotriptycene in 6.5% yield.

Attention was then focused on the original objective of the investigation, namely, the thermal behaviour of 2. The preparation of 2 was accomplished by reaction of benzyne, generated from 9, with 1 as aforementioned.

The reported observation of Beringer and Huang ⁶ that 2 was reduced to 9,10-diphenylanthracene by heating in diglyme at 162° for 2 hours was used as a basis for

the reaction conditions initially employed. Compound 2 was heated under reflux in diglyme solution in the presence of cyclohexene as a potential oxygen trap. Analysis of the mixture by glc after 2.25 hours showed >98% recovery of cyclohexene and no other visible component. Compound 2 was recovered in 90% yield.

The thermal stability of 2 and also of the nitro analog, 20, was therefore investigated. These compounds were independently heated in triglyme at ca 225° for 2.5 hours. Compounds 2 and 20 were recovered in 92% and 91% yield, respectively.

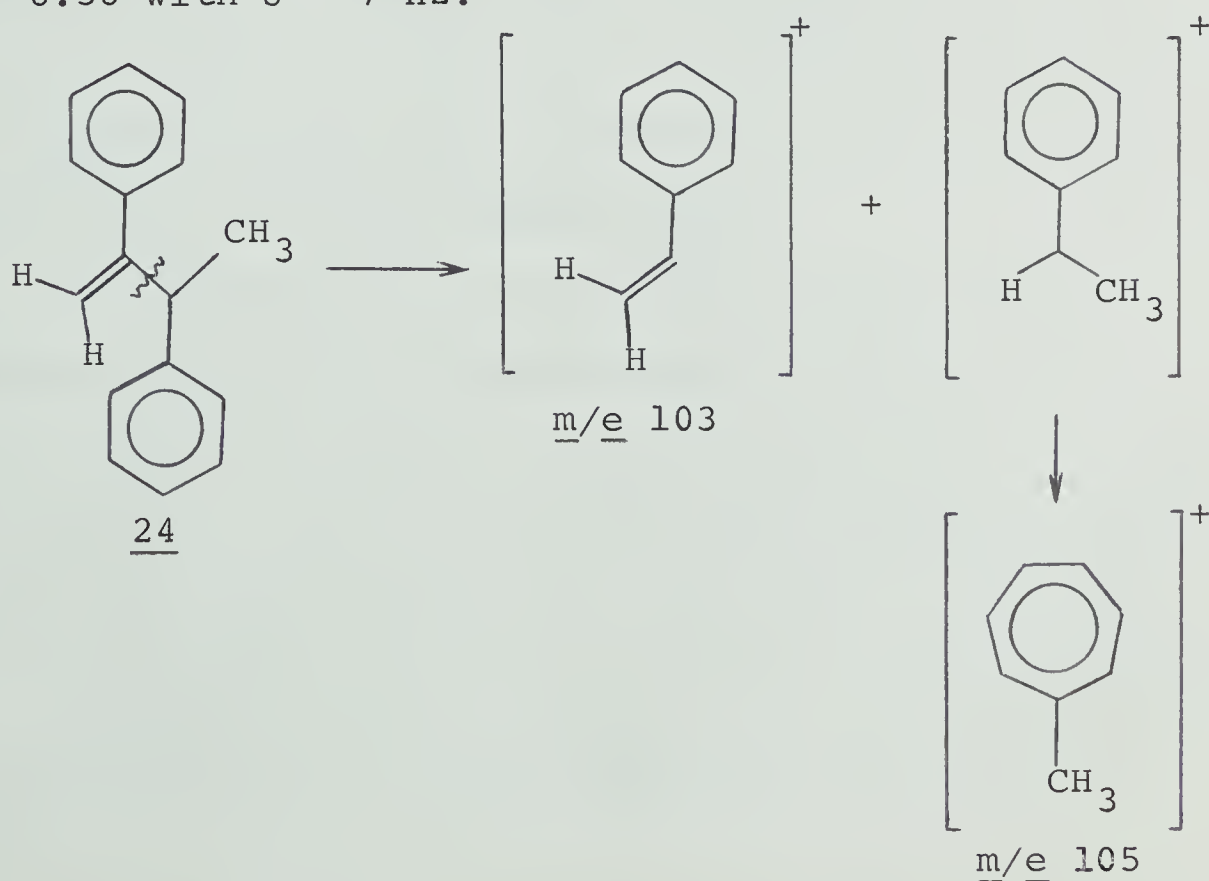
However, it is well known ²⁴ that the presence of a suitable acceptor may induce a radical reaction to occur which would not occur with the substrate alone.

It was felt that a similar molecule-induced homolysis might occur if 2 was heated with $\alpha\beta$ -dimethylstilbene as the potential acceptor. This alkene has a tetrasubstituted double bond and two allylic carbon atoms.

α -Chloroethylbenzene (25) was prepared by the addition of anhydrous hydrogen chloride to styrene.²⁵ An ethereal solution of 25 was added to a stirred suspension of sodium amide in liquid ammonia as described by Brasen et al.²⁶ A mixture of cis- and trans- $\alpha\beta$ -dimethylstilbenes (27 and 28) was obtained in the ratio 63:37 by distillation of the crude reaction product, which had been shown by glc to contain a third component.

The distillation residue was chromatographed over neutral alumina and the third component was isolated by preparative glc. It was identified as 2,3-diphenylbutene-1 (24) by spectroscopy.

The infrared spectrum exhibited olefinic, aromatic and aliphatic carbon-hydrogen stretching frequencies. A band at 1625 cm^{-1} indicated the presence of a conjugated double bond, which was gem-disubstituted as shown by absorption at 902 cm^{-1} . The nmr spectrum showed a multiplet centered at $\tau\ 2.86$ corresponding to the ten phenyl protons, while a pair of single proton singlets at $\tau\ 4.68$ and 4.92 were attributed to the non-equivalent vinylic protons. The benzylic proton at C-3 gave rise to a quartet centred at $\tau\ 6.05$ with $J = 7\text{ Hz}$ and was coupled to the methyl group which produced a three proton doublet at $\tau\ 8.58$ with $J = 7\text{ Hz}$.



The structure was further confirmed by elemental analysis and mass spectroscopy. The mass spectrum exhibited a molecular ion at m/e 208 and a pair of base peaks at m/e 105 and 103. The latter fragments are easily assigned to the corresponding portions from fission α to the styrene double bond.

The ultraviolet spectrum exhibited a maximum at 235 $m\mu$ ($\epsilon = 8,400$), which is in reasonable agreement with the reported ²⁷ value of 243 $m\mu$ ($\epsilon = 10,800$) for 2-phenylpropene.

Although Brasen et al ²⁶ noted an oil as a co-product in this reaction, they merely presumed the structure was 24 or the isomeric 1-methyl-1,2-diphenylcyclopropane.

The mechanism of formation of these three products is explicable in terms of the self-alkylation of 25 under the action of the base to initially form 2-chloro-2,3-diphenylbutane (26), which was isolated by Brasen et al ²⁶ by using less sodium amide.

β -Elimination can then occur by two pathways. Elimination of the activated benzylic proton would result in the formation of $\alpha\beta$ -dimethylstilbenes whereas elimination of one of the three methyl hydrogens would produce the thermodynamically less stable alkene, 24.

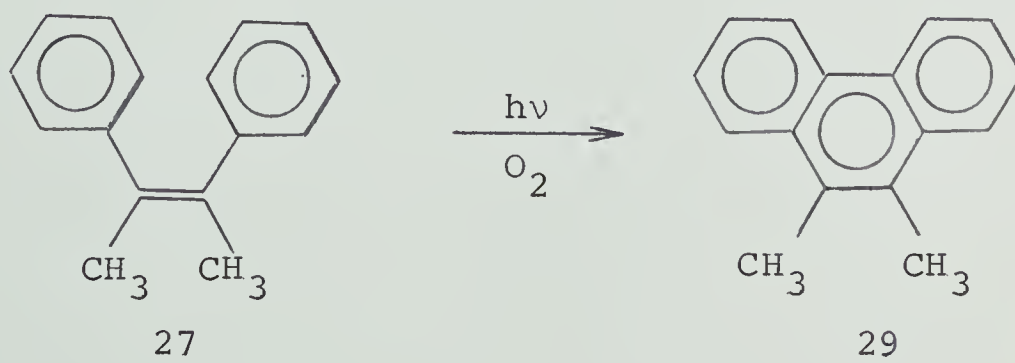
Equimolar amounts of 2 and the mixture of 27 plus 28 were heated at reflux in triglyme solution for 15 hours.

After this time the stilbenes were estimated by glc to be present in 98% of their original concentration in the bright blue fluorescent solution.

A sample of the stilbenes was recovered by preparative glc and nmr spectroscopy was used to confirm their structures. The ratio of 27:28 was estimated to be 56:64 from the nmr spectrum indicating that some thermal isomerisation of the alkene had taken place.

The ultraviolet spectrum was consistent with unchanged 2 and only a weak shoulder was visible at 257 mμ where 9,10-diphenylanthracene exhibits an absorbance maximum.

The reaction mixture was chromatographed over neutral alumina after removal of triglyme. A mixture of 27 and 28 was obtained in the initial eluant followed by a good recovery of 2. The sample of 27 and 28 obtained had a bright blue fluorescence although nmr spectroscopy showed that the stilbenes were >98% pure. It is felt that this fluorescence may be due to the formation of a small amount of 9,10-dimethylphenanthrene (29) from 27 under the influence of incident radiation and in the presence of trace oxygen. ²⁸



In conclusion these results indicate a much greater degree of thermal stability of 2 than had been anticipated from the report of Beringer and Huang.⁶ However this result adds extra weight to the general statement of Stark and Duke ²⁹ that "Reactions proceeding with extrusion of a single atom of oxygen are uncommon,.....".

E X P E R I M E N T A L

Ultraviolet (uv) spectra were determined using a Perkin-Elmer Ultraviolet Spectrophotometer Model 202.

Infrared (ir) spectra were recorded using a Perkin-Elmer 337G, Perkin Elmer 421G or Unicam SP200G Infrared Spectrophotometer.

Nuclear magnetic resonance (nmr) spectra were recorded on a Varian A-60 or HR-100 Spectrometer. Unless otherwise stated deuteriochloroform (CDCl_3) was employed as the solvent with tetramethylsilane (TMS) as the internal reference. Chemical shifts are reported as τ values relative to TMS = 10. The following abbreviations are used in the text: s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet.

Mass spectra were recorded on an AEI Model MS-2 or Model MS-9 Spectrometer.

Gas-liquid chromatography (glc) was performed using an Aerograph A-90-P3 and a Varian Aerograph Series 1200 instrument.

Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected.

Refractive indices were measured on a Bausch and Lomb Abbé-3L Refractometer.

3-Phenylphthalide (5)¹⁰ - 2-Benzoylbenzoic acid (150g; 0.66 mole) was dissolved in glacial acetic acid: water (1500 ml; 4:1 by volume) and zinc dust (300g; 4.62g atom)

was added. The mixture was heated under reflux for 2 hours, then the supernatant liquid was decanted and allowed to cool. The resultant crystals were filtered, washed with sodium bicarbonate (10% w/v), filtered again and finally crystallised (ethanol) to give 3-phenylphthalide, mp 115-117° (lit³⁰ 115-116°), 72% yield.

1,3-Diphenylisobenzofuran (1)¹¹ - Phenylmagnesium bromide (from bromobenzene (0.67 mole)) in ether was added slowly to a stirred solution of 3-phenylphthalide (99g; 0.47 mole) in tetrahydrofuran (THF): diethyl ether (720 ml; 5:1 by volume). After addition of 2N hydrochloric acid (50 ml), the aqueous phase was separated, extracted with THF: ether and then discarded. The combined organic phase was concentrated, and 105g product was obtained in three crops. Recrystallisation (benzene:ethanol; 1:1 by volume) afforded yellow, fluorescent crystals of 1,3-diphenylisobenzofuran, mp 127-128° (lit¹¹ 130-131°, ⁸ 127-128°, ³¹ 125°), 74% yield.

Attempted Preparation of 2-Phenyliodonobenzoate (2)⁶ - 2-Iodobenzoic acid (49.6g; 0.20 mole) was heated with fuming nitric acid (33 ml) and concentrated sulfuric acid (67 ml) at 100° for 1 hour, as described by Beringer and Huang.⁶ The product was obtained as a colorless solid, mp 195-198° (46.4g).

This latter product (26.4g) was condensed with benzene in the presence of sulfuric acid and the resulting iodonium salts were treated with aqueous sodium hydroxide, as des-

cribed by the above authors, to yield the betaine salt.

The product was recrystallised from chloroform:methanol (30:70 by volume) to give colorless crystals, mp 220-221° dec (15.4g).

uv max (H_2O) 205 m μ (ϵ = 17,400), 266 m μ (ϵ = 10,500);
ir (KBr) 3100, 3050, 1625, 1522, 1400, 1342, 1338, 1005,
990, 817, 735, 721 and 685 cm^{-1} ; nmr (DMSO- d_6) τ 1.34
(d,1, J=2.5 Hz), 1.73(m,3), 2.23(m,3), 3.06(d,1, J=8.5 Hz).

5-Nitro-2-Iodosobenzoic Acid (12) and 3-Nitro-2-Iodobenzoic Acid (17). - 2-Iodobenzoic acid (4.96g; 20 mmole) was heated at 100° for 1 hour in a mixture of concentrated sulfuric acid (6.7 ml) and fuming nitric acid (3.3 ml). After cooling, the mixture was poured into ice-water and the resultant precipitate was filtered, washed with water and dried to give pale yellow crystals (5.28g). Fractional crystallisation from water afforded two components, the first of which was 5-nitro-2-iodosobenzoic acid (3.32g) as colorless crystals, mp 229-229.5° dec, 54% yield.

uv max (H_2O) 207 m μ (ϵ = 23,400), 272 m μ (ϵ = 7,080);
ir (Nujol) 1616 (C=O of a 2-iodosobenzoic acid)⁴, 1523
and 1348 cm^{-1} (NO_2); nmr (DMSO- d_6) AMX system, τ 1.24,
1.38 and 1.85, J_{MX} =0.5 Hz, J_{AX} =9 Hz and J_{AM} =2.5 Hz.

Analysis: Calcd for $C_7H_4NIO_5$: C, 27.18; H, 1.30; N, 4.53; I, 41.08. Found: C, 27.11; H, 1.31; N, 4.37; I, 41.38.

The molecular weight was determined by the iodometric titration method of Twiss and Heinzelmann²⁰ as 311.6

(Calcd for $C_7H_4NIO_5$: 309.0).

The second crop of crystals was identified as 3-nitro-2-iodobenzoic acid and was obtained as pale yellow crystals (0.90g), mp 174-207° dec (lit²¹ 204-205.5°) in 15% yield.

ir (Nujol) 1710 (C=O of acid), 1540 and 1374 cm^{-1} (NO_2); nmr (DMSO- d_6) AMX system, τ 2.09, 2.19 and 2.35, $J_{AM}=2$ Hz, $J_{AX}=7$ Hz and $J_{MX}=8$ Hz.

Analysis: Calcd for $C_7H_4NIO_4$: C, 28.69; H, 1.37; N, 4.77; I, 43.31. Found: C, 28.67; H, 1.55; N, 4.69; I, 43.43.

5-Nitro-2-iodosobenzoic acid (200 mg) was treated with an excess of acidified (H_2SO_4) potassium iodide and heated to reflux for 5 min. The solution was filtered while hot, then cooled. The resultant solid was recrystallised (water) to give colorless crystals of 5-nitro-2-iodobenzoic acid (120 mg), mp 194-197° (lit¹⁷ 194°, ¹⁸ 197-198°)

ir (Nujol) 1710 (C=O of acid), 1525 and 1345 cm^{-1} (NO_2); nmr (DMSO- d_6) AMX system, τ 1.56, 1.69 and 1.98, $J_{AM}\sim 0.4$ Hz, $J_{AX}=2.7$ Hz and $J_{MX}=8.7$ Hz.

3-Nitro-2-iodobenzoic acid (90 mg) was treated as above for 5-nitro-2-iodosobenzoic acid and afforded colorless crystals, mp 206-208° having ir and nmr spectra identical to those obtained for 3-nitro-2-iodobenzoic acid.

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3-Nitro-2-Iodobenzoic Acid (17) - 3-Nitrophthalic acid (10.6g; 50 mmole) was converted to anhydro-2-hydroxy-

mercuri-3-nitrobenzoic acid by the procedure of Whitmore and Culhane.²² The mercury compound was then converted to 3-nitro-2-iodobenzoic acid without further purification, by the method of Culhane.²¹ 3-Nitro-2-iodobenzoic acid was obtained as pale yellow crystals, mp 209-211° (lit²¹ 204-205.5°) in 42% yield.

The ir and nmr spectra were identical to those obtained for 3-nitro-2-iodobenzoic acid from the reaction of 2-iodobenzoic acid with $\text{HNO}_3 - \text{H}_2\text{SO}_4$.

5-Nitro-2-Phenyliodonibenzoate (18). - 5-Nitro-2-iodobenzoic acid (3.32g; 10.7 mmole) was dissolved in concentrated sulfuric acid (10 ml) at 0-5° and benzene (10 ml) was then added. The mixture was stirred for 4 hours at room temperature and then poured into ice-water. The crystalline iodonium bisulfate was collected. Addition of a saturated solution of potassium iodide (4 ml) to the filtrate precipitated the bright yellow iodonium iodide, which was also collected. The combined iodonium salts were stirred vigorously with 5N sodium hydroxide solution (10 ml) to afford a tan precipitate. This was filtered, washed with water and dried to give 5-nitro-2-phenyliodonibenzoate, which was recrystallised (chloroform: methanol; 30:70 by volume) to give colorless crystals, mp 220-221° dec, 68% yield.

The uv and ir spectra were virtually identical to those obtained for the product obtained in the attempted

preparation of 2-phenyliodonobenzoate.

Analysis: Calcd for $C_{13}H_8NO_4$: C, 42.29; H, 2.18; N, 3.80; I, 34.37. Found: C, 42.39; H, 2.22; N, 3.76; I, 34.24.

6-Nitro-1,2,3,4-Tetraphenylnaphthalene (21). - 2,3,4,5-Tetraphenylcyclopentadienone³² (0.50g; 1.3 mmole) and 5-nitro-2-phenyliodonobenzoate (0.55g; 1.5 mmole) were placed in a boiling tube with triglyme (6 ml). The mixture was heated to 200-205° for a few minutes until the solution became clear. After cooling to ca 90°, 95% ethanol (10 ml) was added, followed by the dropwise addition of water until a faint permanent precipitate was formed. The solution was then cooled in an ice-bath and the resultant precipitate was collected to give 6-nitro-1,2,3,4-tetraphenylnaphthalene (0.52g) as bright yellow crystals in 86% yield. Recrystallisation (chloroform:methanol) yielded yellow crystals, mp 275-277°.

(The above method was analogous to that of Fieser¹⁴ for the preparation of 1,2,3,4-tetraphenylnaphthalene).

uv max (95% EtOH) 208 mμ ($\epsilon = 53,500$), 231 mμ ($\epsilon = 38,000$), 279 mμ ($\epsilon = 29,500$); ir (Nujol) 1522 and 1339 cm^{-1} (NO_2); nmr τ 1.35(d of d, 1, $J=0.5$, 2.5 Hz), 1.87(d of d, 1, $J=2.5$, 8.5 Hz), 2.22(d of d, 1, $J=0.5$, 8.5 Hz), 2.75 (m, 10), 3.13(m, 10); mass spectrum m/e 477 (corresponds to $C_{34}H_{23}NO_2$), 447, 78 (base), 77, 52, 51.

Analysis: Calcd for $C_{34}H_{23}NO_2$: C, 85.51; H, 4.85; N,

2.93. Found: C, 85.34; H, 5.10; N, 2.80.

2-Nitro-9,10-Epoxy-9,10-Diphenyl-9,10-Dihydroanthracene (20). - To a solution of 1,3-diphenylisobenzofuran (1.35g; 5 mmole) in refluxing triglyme (38 ml) under nitrogen, was added 5-nitro-2-phenyliodonobenzoate (3.16g; 9 mmole) in small portions. After the addition (ca 12 min) the mixture was maintained at reflux for a further 3 min. The majority of the solvent was then removed under reduced pressure (1 mm). Addition of water caused precipitation of a solid (2.80g), which was chromatographed over Florisil using petroleum ether as eluant to give 2-nitro-9,10-epoxy-9,10-diphenyl-9,10-dihydroanthracene. Recrystallisation (benzene:methanol) afforded very pale yellow crystals, mp 189-190° in 54% yield.

uv max (95% EtOH) 216 mμ ($\epsilon = 22,900$), 244 mμ ($\epsilon = 9,300$), 290 mμ ($\epsilon = 4,170$); ir (Nujol) 1522 and 1340 cm^{-1} (NO_2); nmr τ 1.94(d,1, $J=2$ Hz), 2.15(m,5), 2.60(m,9), 3.03(m,2); mass spectrum m/e 391 (corresponds to $\text{C}_{26}\text{H}_{17}\text{NO}_3$), 374, 344, 239, 105 (base), 77.

Analysis: Calcd for $\text{C}_{26}\text{H}_{17}\text{NO}_3$: C, 79.78; H, 4.38; N, 3.58. Found: C, 79.99; H, 4.34; N, 3.70.

2-Nitrotriptycene (22). - 5-Nitro-2-phenyliodonibenzoate (1.85g; 5 mmole) was added to a refluxing solution of anthracene (0.89g; 5 mmole) in triglyme (10 ml). After 3 min excess anthracene was removed by addition of maleic

anhydride (0.49g; 5 mmole) refluxing for 5 min and then treatment with ethanolic potassium hydroxide. Upon cooling in an ice-bath crystals appeared which were filtered and washed with aqueous methanol. The precipitate was dried to give tan crystals in 43% yield, which were recrystallised (methylene dichloride:methanol) to give 2-nitrotriptycene, mp 277-279° (lit ²³ 270-271°).

ir (Nujol) 1517 and 1340 cm^{-1} (NO_2); nmr τ 1.80 (d,1, $J=2.5$ Hz), 2.08(d of d,1, $J=2.5$, 8.5 Hz), 2.57 (m,5), 2.92(m,4), 4.48(s,2); mass spectrum m/e 299 (Calcd for $\text{C}_{20}\text{H}_{13}\text{NO}_2$:299.0946. Found: 299.0949), 253, 252 (base), 250, 126.

Analysis:Calcd for $\text{C}_{20}\text{H}_{13}\text{NO}_2$: C, 80.25; H, 4.38; N, 4.68. Found: C, 80.04; H, 4.32; N, 4.93.

2-Phenyliodonobenzoate (9).¹⁴ - 2-Iodobenzoic acid

(10.0g; 40 mmole) was converted to 2-phenyliodonibenzoate by the method of Fieser and Haddadin.¹⁴ The betaine salt was obtained as colorless crystals, mp 226-227° dec (lit ¹⁴ 220° dec) in 78% yield.

uv max (H_2O) 207 $m\mu$ ($\epsilon = 24,000$), 226 $m\mu$ (shoulder); ir (KBr) 1610 and 1347 cm^{-1} (C=O of carboxylate anion); nmr ($\text{DMSO}-d_6$) τ 1.86(m,3), 2.46(m,5), 3.32(m,1).

Analysis:Calcd for $\text{C}_{13}\text{H}_{11}\text{IO}_3$: C, 45.61; H, 3.21; I, 37.13. Found: C, 45.37; H, 3.12; I, 37.12.

1,2,3,4-Tetraphenylnaphthalene (11).¹⁴ - 2,3,4,5-Tetra-

phenylcyclopentadienone ³² (1.0g; 2.6 mmole) was reacted with

2-phenyliodonioibenzoate (1.0g: 2.9 mmole) as described for the preparation of 6-nitro-1,2,3,4-tetraphenylnaphthalene. White crystals of 1,2,3,4-tetraphenylnaphthalene, mp 205-207° (lit ¹⁴ 203-204°, ³⁵ 204-206°) were obtained in 74% yield.

uv max (95% EtOH) 204 mμ ($\epsilon = 66,000$), 216 mμ ($\epsilon = 64,600$), 241 mμ ($\epsilon = 66,000$), 297 mμ ($\epsilon = 13,900$); mass spectrum $\underline{m}/\underline{e}$ 432 (base) (corresponds to $C_{34}H_{24}$), 355, 353, 177.

Analysis: Calcd for $C_{34}H_{24}$: C, 94.41; H, 5.59. Found: C, 94.51; H, 5.72.

9,10-Epoxy-9,10-Diphenyl-9,10-Dihydroanthracene (2). 1,3-Diphenylisobenzofuran (4.0g; 15 mmole) was reacted with 2-phenyliodonioibenzoate (5.5g; 16 mmole) as described for the preparation of 6-nitro-1,2,3,4-tetraphenylnaphthalene. 9,10-Epoxy-9,10-diphenyl-9,10-dihydroanthracene was obtained as colorless crystals, mp 190-192° (lit ⁸ 188 - 188.5°) in 87% yield. Recrystallisation (benzene:ether: methanol) caused no change in melting point.

uv max (petrol ether) 220 mμ ($\epsilon = 38,000$); nmr τ 2.02(m,4), 2.54(m,10), 3.01(m,4); mass spectrum $\underline{m}/\underline{e}$ 346 (Calcd for $C_{26}H_{18}O$: 346.1359. Found: 346.1357), 241, 239, 105 (base), 77.

Analysis: Calcd for $C_{26}H_{18}O$: C, 90.14; H, 5.24. Found: C, 90.25; H, 5.11.

A sample of the product was reduced by refluxing with

zinc dust in glacial acetic acid for 20 min.⁸ 9,10-Diphenylanthracene was obtained as pale yellow crystals, mp 246-249° (lit³³ 249-250°) in 68% yield. The product exhibited an infrared spectrum identical to that of an authentic sample of 9,10-diphenylanthracene.

9,10-Peroxy-9,10-Diphenyl-9,10-Dihydroanthracene (3)⁹ - 9,10-Diphenylanthracene (1.0g; 3 mmole) was dissolved in carbon disulfide (100 ml) and the solution cooled in an ice-bath. The solution was irradiated with a sunlamp (GE: 250 watt), while air was being bubbled through. After 6 hours no starting material could be detected (tlc). The solution was evaporated and the residue was crystallised twice (benzene) and finally chromatographed over neutral alumina using petroleum ether as eluant. The peroxy product was obtained as white crystals, mp 179-180° dec (gas evolved then resolidified and remelted 249-251° (lit³³ 9,10-diphenylanthracene, mp 249-250°)) in 32% yield.

Attempted Reduction of 9,10-Peroxy-9,10-Diphenyl-9,10-Dihydroanthracene (3). - The peroxy compound (200 mg) was dissolved in toluene (10 ml) and triphenylphosphine (420 mg) was added. The mixture was heated on a steam bath for 65 hours, when the reaction product was shown (tlc) to consist mainly of 9,10-diphenylanthracene and triphenylphosphine oxide.

α -Chloroethylbenzene (25)²⁵ - Hydrogen chloride gas was passed into a vigorously stirred solution of styrene (39.5g;

0.38 mole) under 30 mm Hg pressure for 10 hours. The mixture was distilled to give a colorless liquid, bp 64-72°/11 mm (35.5g), which was redistilled to afford α -chloroethylbenzene, bp 69-71°/11 mm, n_D^{20} 1.5286 (lit ²⁵ 72°/11 mm, ³⁴ n_D^{20} 1.5294) in 45% yield.

nmr (CCl₄) τ 2.72(m,5), 5.03(q,1, J=7 Hz), 8.22(d,3, J=7 Hz).

$\alpha\beta$ -Dimethylstilbene (27 and 28) ²⁶ and 2,3-Diphenylbutene-1 (24). - A solution of α -chloroethylbenzene (23.5g; 0.17 mole) in anhydrous ether (100 ml) was added to a stirred suspension of sodium amide (7.0g; 0.18 mole) in liquid ammonia (170 ml) as described by Brasen et al.²⁶ The crude reaction product contained three components as revealed by glc. Distillation (Nester-Faust spinning band column, 60 cm x 1 cm) afforded a mixture of cis and trans $\alpha\beta$ -dimethylstilbenes, bp 68-82°/0.3 mm. Trituration of the distillate with methanol afforded a solid. Recrystallisation (MeOH) gave colorless crystals, mp 46-49° (lit ²⁶ cis 66°, trans 107°).

ir (CCl₄): 3090 - 3030 (aromatic CH), 2990 - 2865 (aliphatic CH), 1673 (C=C), 1600, 1493 and 1445 cm⁻¹ (aromatic); nmr: τ 3.06(s,5), 7.86(s,3) cis, τ 2.77(s,5), 8.13(s,3) trans. cis:trans = 63:37.

The residue from the distillation was chromatographed over neutral alumina using petroleum ether as eluant and further purified by preparative glc (10% neopentyl glycol

sebacate, 180°) to yield a colorless oil, n_D^{20} 1.5806, which was identified as 2,3-diphenylbutene-1.

uv max (hexane): 235 mμ ($\epsilon = 8,400$); ir (thin film): 3090 - 3030 (aromatic and olefinic CH), 2975 - 2880 (aliphatic CH), 1625 (conjugated C=C), 902 cm^{-1} (gem-disubstituted C=C); nmr (CCl_4): τ 2.86(m,10), 4.68(s,1), 4.92(s,1), 6.05(q,1, $J=7$ Hz), 8.58(d,3, $J=7$ Hz); mass spectrum m/e 208 (corresponds to $\text{C}_{16}\text{H}_{16}$), 193, 130, 115, 105, 103 (base), 91, 77, 51.

Analysis: Calcd for $\text{C}_{16}\text{H}_{16}$: C, 92.26; H, 7.74. Found: C, 92.14; H, 7.83.

Thermal Behaviour of 9,10-Epoxy-9,10-Diphenyl-9,10-Dihydroanthracene (2). - The epoxy compound (200 mg) was dissolved in triglyme (5 ml). The solution was heated at reflux (ca 225°) for 2.5 hours under nitrogen, then cooled to 90° and ethanol (3 ml) was added. The solution was reheated to boiling and water added dropwise until a faint, permanent precipitate was formed. On cooling, the solution yielded colorless crystals, mp 190-192° (186 mg). The absence of 9,10-diphenylanthracene was confirmed (tlc) and the product was recrystallised (cyclohexane) to give colorless crystals, mp 191-192°.

Analysis: Calcd for $\text{C}_{26}\text{H}_{18}\text{O}$: C, 90.14; H, 5.24. Found: C, 89.86; H, 5.33.

Thermal Behaviour of 2-Nitro-9,10-Epoxy-9,10-Diphenyl-9,10-Dihydroanthracene (20). - The nitroepoxy compound was

treated as for the un-nitrated derivative above. Pale yellow crystals, mp 187-189° (182 mg) were recovered and recrystallised (benzene:methanol, 1:2 by volume) to give starting material, mp 190-190.5°.

Analysis: Calcd for $C_{26}H_{17}NO_3$: C, 79.78, H, 4.38; N, 3.58. Found: C, 79.88; H, 4.45; N, 3.46.

Thermal Behaviour of 9,10-Epoxy-9,10-Diphenyl-9,10-Dihydroanthracene (2) in Presence of Cyclohexene. - Cyclohexene

(0.82 g; 10 mmole) and diglyme (10 ml) were placed in a 50 ml 3-necked flask, fitted with a gas inlet tube and condenser; the latter was connected to a cold finger filled with Dry Ice-acetone. Nitrogen was bubbled through the solution prior to and for a few minutes after the addition of 9,10-epoxy-9,10-diphenyl-9,10-dihydroanthracene (0.35 g; 1 mmole). The mixture was then heated to reflux under nitrogen for 2.25 hours. The temperature of the flask contents were measured as 146°.

Analysis by glc (10% Squalane, 100°) showed almost complete recovery of cyclohexene (> 98%) and no other visible volatile products.

The clear, colorless solution was distilled to ca half volume and then ethanol (5 ml) was added. The solution was reheated to boiling and water added dropwise until a faint, permanent precipitate was formed. The solution was cooled to afford colorless crystals, mp 188-190° (0.315 g). The product was recrystallised

(cyclohexane) to give colorless crystals, mp 191-192°.

Analysis: Calcd for $C_{26}H_{18}O$: C, 90.14; H, 5.24.

Found: C, 90.02; H, 5.23.

Thermal Behaviour of 9,10-Epoxy-9,10-Diphenyl-9,10-Dihydroanthracene (2) in Presence of $\alpha\beta$ -Dimethylstilbenes (27 and 28). - The epoxy compound (0.692g; 2 mmole) and cis and trans- $\alpha\beta$ -Dimethylstilbenes (0.416g; 2 mmole) were dissolved in triglyme (20 ml). Nitrogen was bubbled through the solution to remove dissolved air while the temperature was raised. The mixture was finally heated at reflux under nitrogen for 15 hours. Analysis of the reaction mixture by glc (10% neopentyl glycol sebacate (NPGSE); 180°) showed 98% recovery of the stilbenes. A sample of the stilbenes was isolated by preparative glc (15% NPGSE; 190°).

nmr τ 3.08(s,5), 7.86(s,3) cis; τ 2.78(s,5), 8.14(s,3) trans; cis:trans = 56:44.

A sample (10 μ l) of the reaction mixture was diluted to 100 ml and the uv spectrum recorded.

uv max (petrol ether) 218 m μ (A=0.605), 257 m μ (shoulder).

The total reaction mixture was then dissolved in benzene (25 ml) and extracted with water (6 x 50 ml). The organic layer was dried (Na_2SO_4) and evaporated. The residue was chromatographed over neutral alumina using petroleum ether as eluant to afford cis and trans- $\alpha\beta$ -

dimethylstilbenes (blue fluorescence) and 9,10-epoxy-9,10-diphenyl-9,10-dihydroanthracene. The latter was recrystallised (cyclohexane) to give colorless crystals, mp 191-192°.

Analysis: Calcd for $C_{26}H_{18}O$: C, 90.14; H, 5.24.

Found: C, 89.95; H, 5.25.

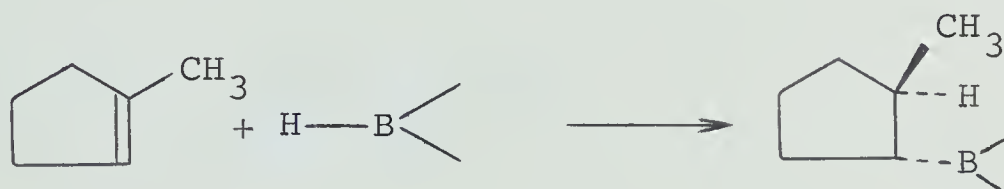
THE UTILITY OF ORGANOBORANES IN ORGANIC SYNTHESIS.
A NOVEL SYNTHESIS OF ALDEHYDES.

I N T R O D U C T I O N

The use of organometallic intermediates in synthesis constitutes an important and rapidly expanding area of organic chemistry.

The comprehensive studies of H. C. Brown and many co-workers have contributed in no small way to this expansion. The increasing utility of organoboron reagents is evident in the number of recently published reports.

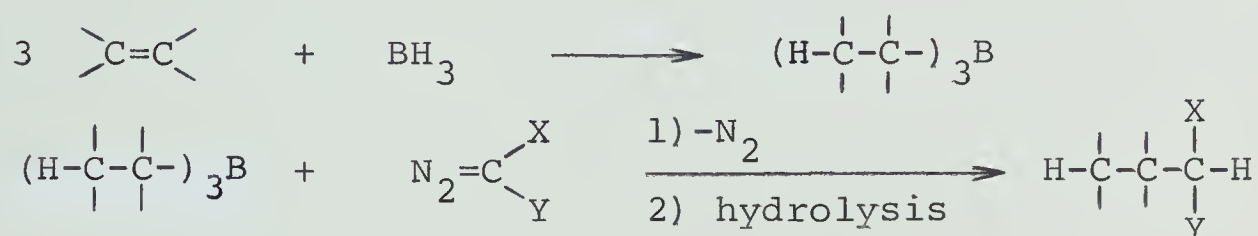
The cis, anti-Markovnikov addition of borane (BH_3) to an alkene has been termed "hydroboration" and the product is known as an organoborane.



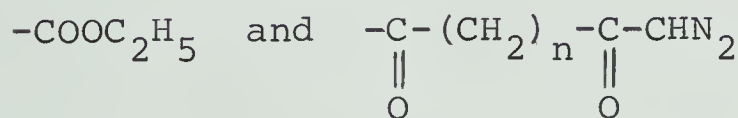
The versatility of trialkylboranes (R_3B) in synthesis is evident in the wide range of transformations which may be accomplished. These include: isomerisation³⁶; displacement³⁶; contrathermodynamic isomerisation of olefins³⁶; cyclisation^{37,38}; protonolysis³⁶; oxidation to alcohols³⁶; oxidation to ketones³⁹; amination⁴⁰; metallation⁴¹; coupling^{42,43}; 1,4 addition to

α, β -unsaturated aldehydes ^{44,45}, ketones ⁴⁶, and Mannich bases ⁴⁷; reaction with ylides ⁴⁸ or with α -halo carbanions ⁴⁹; and carbonylation ⁵⁰ to tertiary alcohols, secondary alcohols, ketones, primary alcohols, aldehydes, ring ketones and polycyclics.

The reactions of trialkylboranes with diazo compounds has been shown by Hooz and Linke ⁵¹ and Hooz and Gunn ⁵² to afford a convenient and simple method of converting an olefin into a functionalised homolog.



where X=H and Y=CH₃-C(=O)-, C₆H₅-C(=O)-, -C≡N,



The purpose of the present work was to investigate the reactions of trialkylboranes with diethyl diazomalonate (X=Y= -COOC₂H₅) and diazoacetaldehyde (X=H, Y=H-C(=O)-) respectively.

In the course of this study a novel preparative method for diazoacetaldehyde was developed.

One of the limitations of the reaction of a trialkylborane with a diazo compound and many other substrates, is utilisation of only one of the three alkyl

groups. Thus the maximum yield, based on the olefin, is necessarily limited to 33.3%. The use of a monoalkyl-dialkoxo-borane (boronic acid diester) instead of a tri-alkylborane was briefly studied in an attempt to circumvent this restriction.

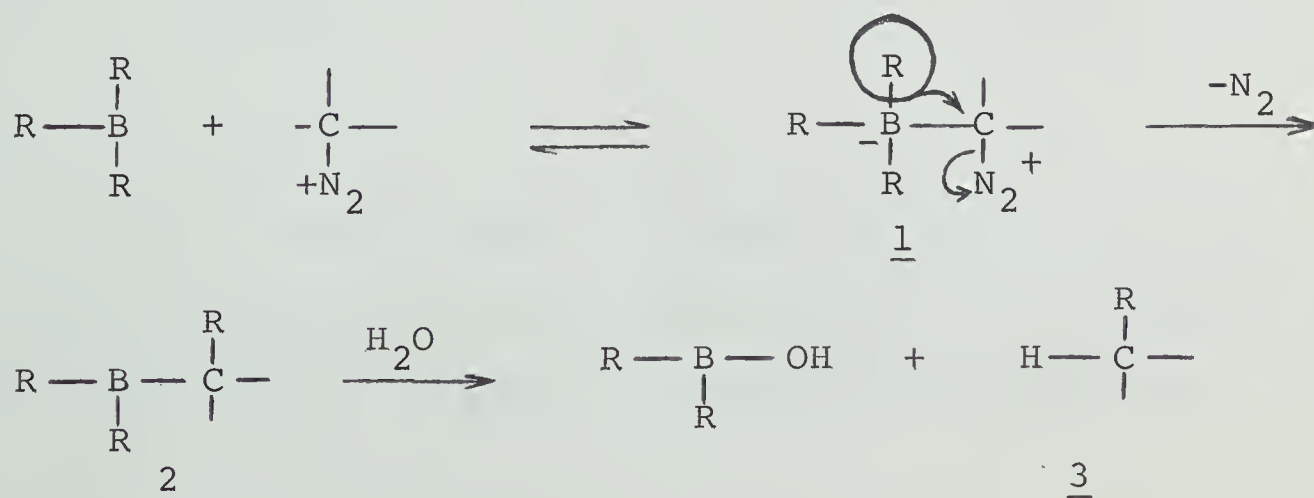
The reactions of trialkylboranes with acyl azides, compounds which are isoelectronic with diazoketones, was also briefly investigated.

R E S U L T S A N D D I S C U S S I O N

Recent work in this laboratory has provided convenient methods for the synthesis of ketones, nitriles, esters⁵¹ and diketones⁵² from olefins via hydroboration and reaction with diazo compounds. The present work was directed towards an extension of this procedure for the diazo compounds, diethyl diazomalonate and diazoacetaldehyde, which by analogy, should produce alkylmalonates and aldehydes, respectively.

Although no mechanistic study had been undertaken, it seemed reasonable to postulate a general mechanism for the above-mentioned reactions by analogy to known processes.

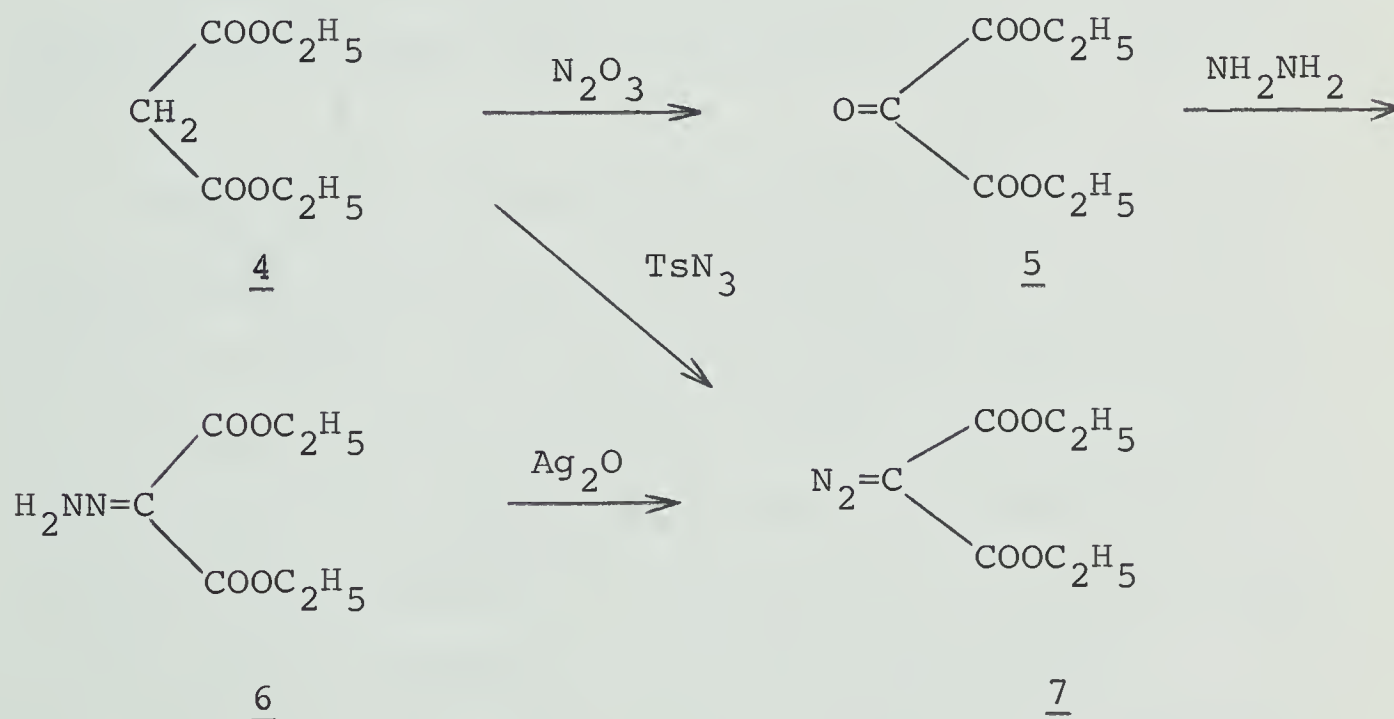
Thus (i) reversible formation of a Lewis acid - Lewis base complex between the electron-deficient boron atom and the nucleophilic carbon of the diazo compound to give 1, followed by (ii) a 1,2-alkyl shift from boron to carbon with the simultaneous, irreversible expulsion of nitrogen to form the intermediate 2 and finally (iii) fission of the boron-carbon bond of this intermediate to form product 3.



Reaction of a Trialkylborane with Diethyl Diazomalonate.

Diethyl diazomalonate (7) was prepared by two routes.

In the first method diethyl malonate (4) was oxidised to the oxomalonate ester (5) by dinitrogen trioxide using the procedure of Dox⁵³ and of Corson and Hazen.⁵⁴ The hydrazone of oxomalonate (6) was prepared and then oxidised with silver oxide as described by Ciganek⁵⁵ to give 7. However the overall yield was only 9%. The infrared spectrum of the product showed a strong absorption at 2140 cm^{-1} characteristic of a diazo function and bands at 1758 and 1736 cm^{-1} attributable to the ester carbonyl.



In the second method the diazo ester (7) was prepared in 67% yield in the single step procedure due to Rosenberger and Yates⁵⁶, by reaction of 4 with *p*-toluenesulfonyl azide

and diethylamine.

A particularly useful feature of the reactions of trialkylboranes with diazo substrates is that the ease and extent of reaction is readily interpreted from observation of the rate and quantity of nitrogen evolved.

Addition of compound 7 to a solution of trihexylborane in THF at 10° resulted in very slow evolution of gas; the temperature was therefore raised to accelerate nitrogen evolution. After 7 hours at reflux temperature the gas was estimated to be 81% of the theoretical amount. This value agreed favorably with the values of 21% and 24% unreacted 4 estimated by ir and glc, respectively.

However, on hydrolysis (KOH - H₂O₂) no diethyl n-hexylmalonate, the expected product, could be observed by glc.

The use of oxidative hydrolysis should cause all boron-bound alkyl groups to be released as the corresponding alcohol. The yield of 1-hexanol was estimated as 57% based on the 1-hexene, thereby indicating the utilisation of a proportion of the boron-bound alkyl groups. (The migration of one alkyl group should produce a 67% yield of alcohol on oxidative hydrolysis).

The lack of desired product prompted the use of a copper catalyst, which is known to catalyse many of the reaction of diazo compounds. However, the addition

of a solution of the diazomalonate (7) to a solution of trihexylborane containing a dispersion of metallic copper resulted in no observable gas evolution at 10°. After 4 hours at reflux only 18% of the theoretical nitrogen had been evolved.

Oxidative hydrolysis was used after removal of the copper, but again none of the desired product could be observed by glc. Both infrared and glc analysis indicated a negligible amount of 7 remained. The yield of 1-hexanol was estimated as 33% based on 1-hexene and the absence of the coupling product, tetracarbethoxyethelene was shown by glc. (The latter product could be expected from the copper-catalysed reaction of 7).

At this stage it was felt that side reactions were removing the diazo substrate before reaction could occur with the borane. Therefore a solution of 7 was added very slowly to a refluxing solution of trihexylborane in THF, in the hope that the desired reaction would take place before the concentration of 7 increased to the extent where reaction between two or more diazo molecules was significant. However, nitrogen evolution after 6 hours at reflux was only 12% of theory.

At about this time an observation was made by Dr. S. Linke⁵¹ that alkaline hydrolysis in the absence of peroxide was sufficient to cause fission of the presumed boron-carbon bond of the functionalised group to form

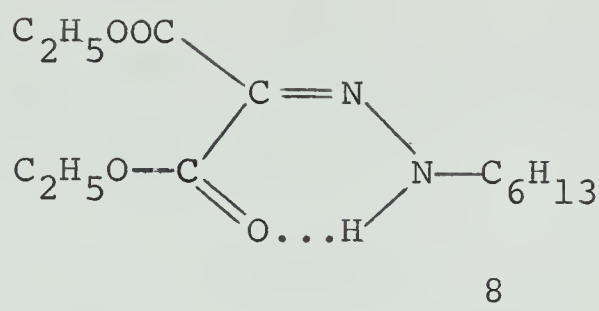
the product and simplified the isolation of product by avoiding the oxidation of boron-bound alkyl groups. In view of this it was decided to work up the reaction by three routes using (a) $\text{KOH-H}_2\text{O}_2$ hydrolysis (b) KOH only and (c) water only.

Using glc it was shown that diethyl n-hexylmalonate was absent from all three products and the yield of 1-hexanol from (a) was 40% based on 1-hexene.

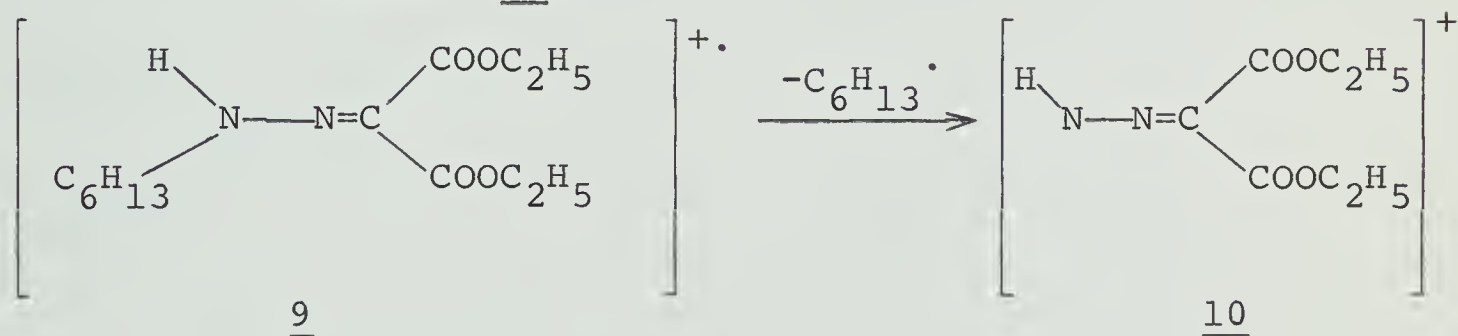
The above evidence of apparent reaction was in conflict with the absence of the desired product or of any other major product observable by glc (10% Carbowax 20M; 150°). However, when the reaction mixtures were re-analysed by temperature programmed glc (Carbowax; 100° - 200° at $12^\circ/\text{min}$) a sizeable, non-Gaussian peak was observed at long retention time for all samples. The peak shape was symptomatic of degradation taking place either in the injection port or on the column itself.

This component was isolated by evaporation of a portion of a reaction mixture, chromatography over Florisil and finally, preparative glc.

The product was identified spectroscopically as the N-n-hexylhydrazone of diethyl oxomalonate (9). The infrared spectrum exhibited the presence of a hydrogen-bonded NH at 3180 cm^{-1} , which may be explained by an intramolecularly bonded species 8.

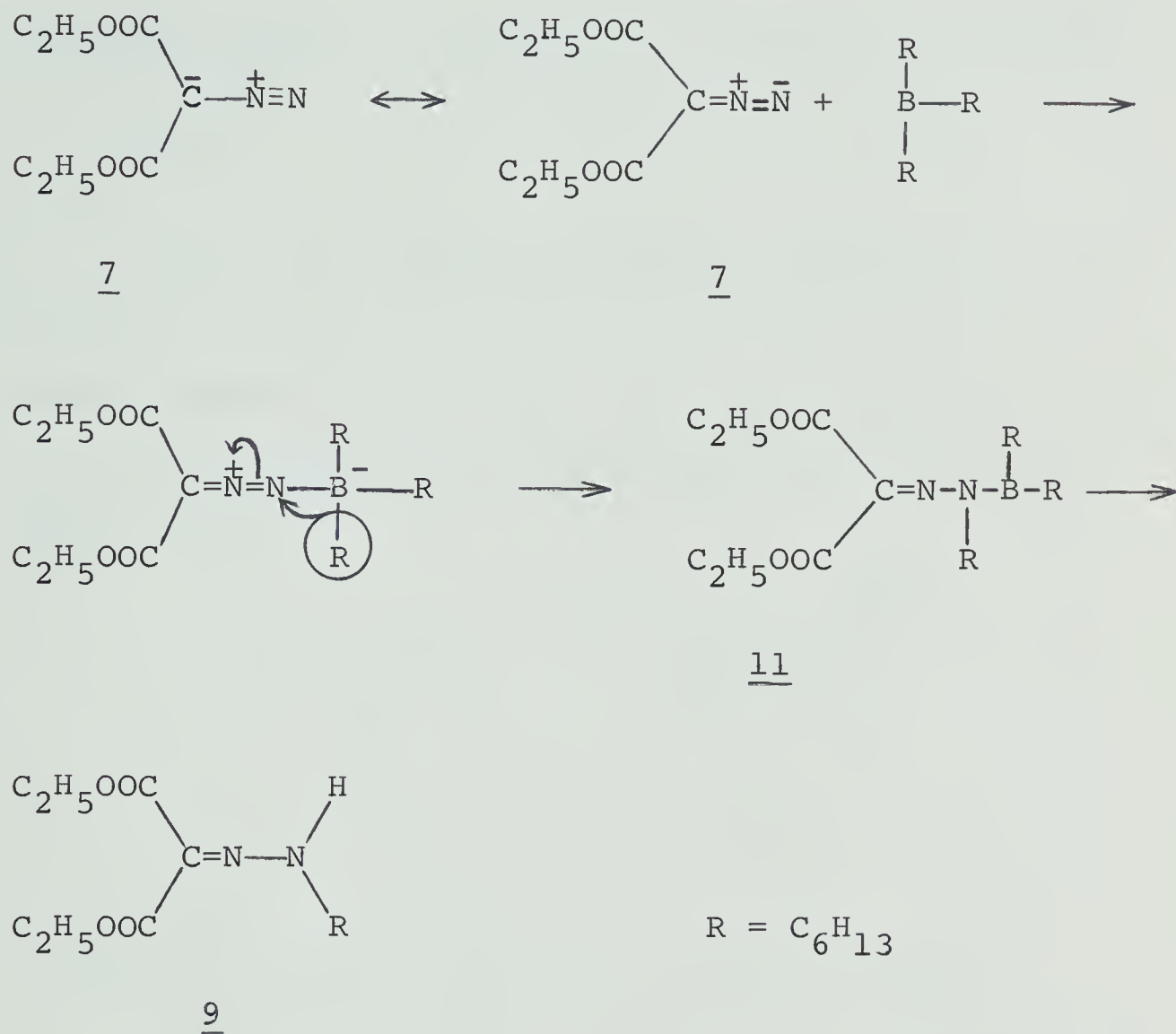


Absorptions at 1710 and 1085 cm^{-1} confirmed the presence of the ester function and the band at 1650 cm^{-1} was attributed to the stretching frequency of the C=N group. The molecular weight was determined as 272.1737 (Calcd for $\text{C}_{13}\text{H}_{24}\text{N}_2\text{O}_4$: 272.1736) by high-resolution mass spectroscopy. The prominent ion at m/e 187 was thought to be due to cleavage of the hexyl group to leave the resonance stabilised fragment (10).



The proposed mechanism for reaction of trialkylboranes with diazo compounds outlined above, postulates the formation of a complex by interaction of the boron atom with the nucleophilic carbon atom of the diazo substrate. The formation of the N-n-hexylhydrazone of diethyl oxomalonate (9) can be explained by (i) interaction of the boron atom with the terminal nitrogen of the diazo group (ii) a 1,2-alkyl migration from boron to nitrogen to form the inter-

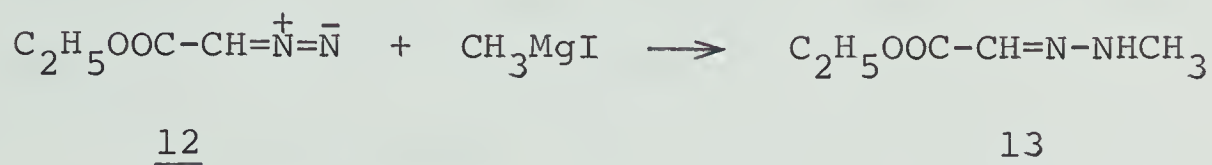
mediate (11) and (iii) fission of the boron-nitrogen bond of 11 to form product (9).



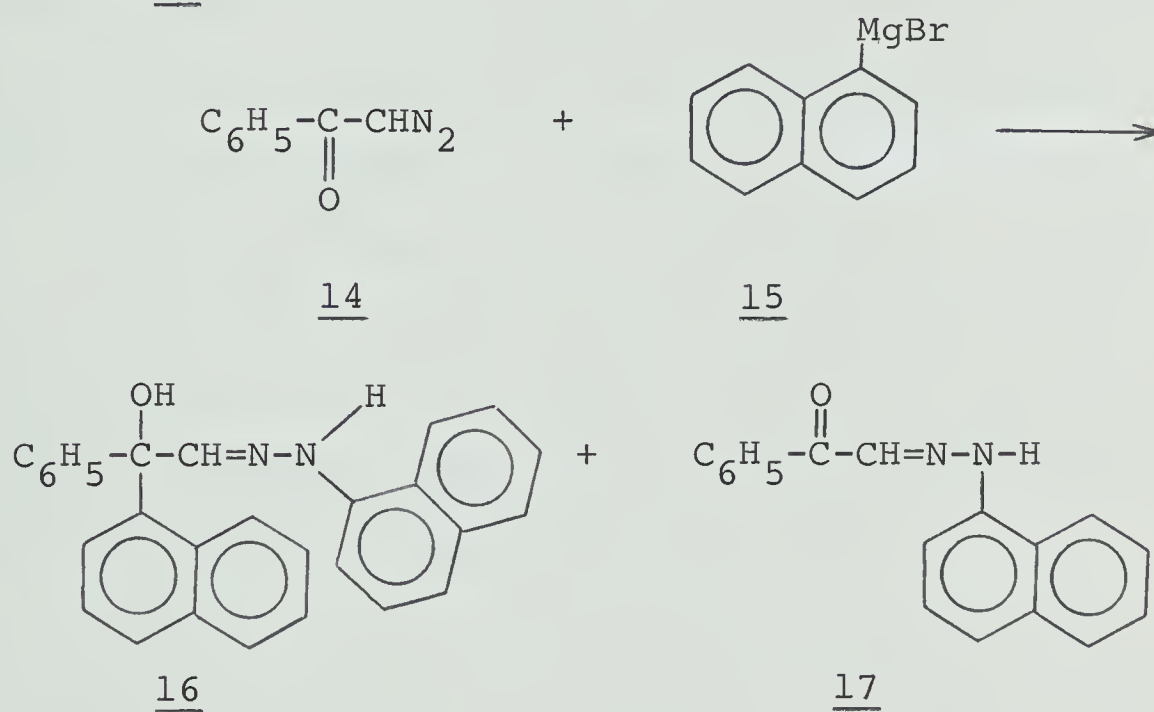
Such a reaction is not without precedent. Thus Gilman and co-workers⁵⁷ have shown that Grignard reagents react with substituted diazomethanes to form the N-substituted hydrazones.

A similar observation was recorded earlier by Zerner⁵⁸ for the reaction of Grignard reagents with diazoacetic ester. Thus reaction of ethyl diazoacetate

(12) with methylmagnesium iodide produced the methyl hydrazone of ethyl glyoxalate (13).



More recent work by Canonica and Tedeschi ⁵⁹ has explored the synthetic utility of these reactions. These workers isolated (16) and (17) from the reaction of 1-naphthylmagnesium bromide (15) with diazoacetophenone (14).



In view of these related reactions of organomagnesium compounds with diazo substrates it was decided to investigate the reaction of n-hexylmagnesium bromide with 7. The substituted hydrazone 8 was isolated from

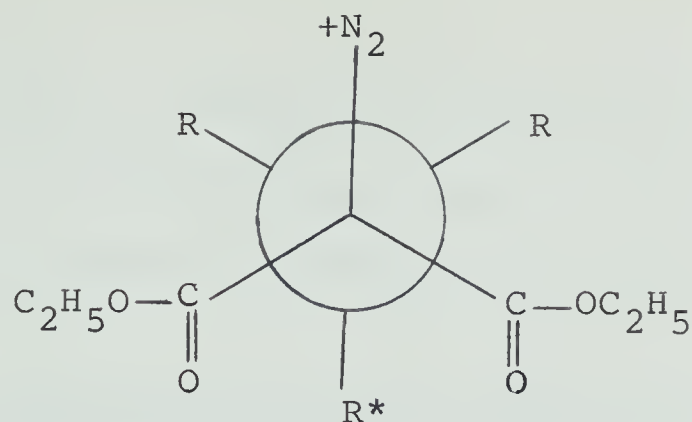
the reaction product and was used as a standard to estimate the yields obtained in the organoborane reactions. These yields were determined as 22%, in the initial reaction^{*}, 14% using copper catalysis, and 11, 20 and 32% from (a), (b) and (c) respectively in the third experiment.

In conclusion, the reaction of trihexylborane with diethyl diazomalonate does not seem to follow the general pathway observed for other diazo compounds with an α -carbonyl or cyano function.

The reactivity of the boron atom in organoboranes appears to be particularly sensitive to steric hindrance. In fact, Brown⁶⁰ has used organoboranes as a sensitive probe in the investigation of the influence of steric factors on the strengths of bases.

It seems reasonable to assume that the migrating alkyl group and the departing nitrogen molecule will be trans coplanar with the reactive carbon atom and therefore a Newman projection (17a) may be drawn to show the complex immediately prior to rearrangement.

^{*}The high yield of evolved nitrogen (81%) in the initial experiment must be erroneous, in view of the nitrogen balance and the substantially lower yields of gas achieved in the other two experiments, and could have been due to a leaking joint.



R^{*} is the migrating alkyl group

It can be seen that R^{*} must approach the carbon atom between the flanking carbethoxy groups resulting in much greater non-bonded interaction than would be experienced in the previously reported ^{51,52} examples where one of the flanking groups was always hydrogen.

The nucleophilicity of the central carbon atom in the diazo compound would be a major factor in the extent of formation of the acid-base complex (1). The presence of two electron-withdrawing groups would markedly reduce the Lewis-base strength of the diazo-malonate (cf acidity of methylene protons in ethyl acetate pK_a ~ 24 and diethyl malonate pK_a 13).⁶¹

The combined effect of these factors would be to cause a retardation of the overall reaction and could thereby allow a competing reaction or reactions to predominate.

Although the yields of hydrazone were low, no

attempt was made to optimise the reaction due to the existence of an equally facile route to these compounds using Grignard reagents and diazo compounds.

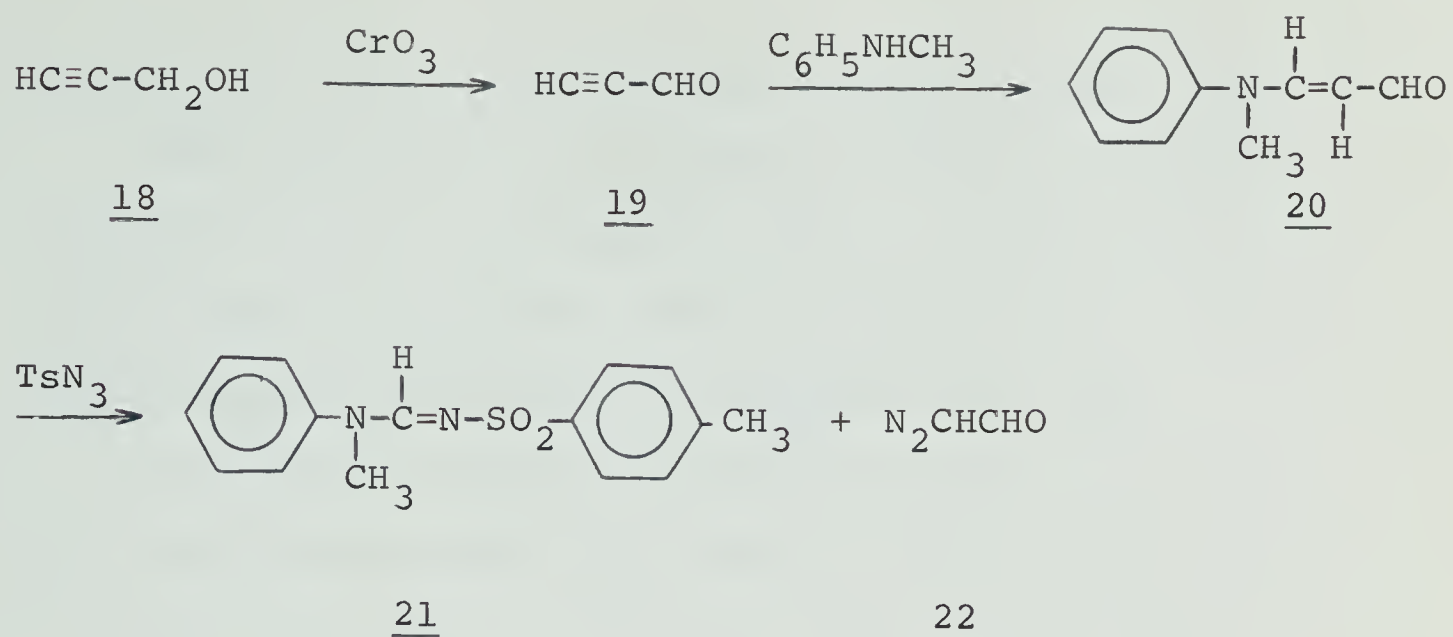
Reaction of Trialkylboranes with Diazoacetaldehyde.

A Novel Synthesis of Aldehydes.

The first preparation of diazoacetaldehyde (22) had only recently been achieved by Arnold ⁶² from β -N-methylanilinoacrolein (20) and excess *p*-toluene-sulfonyl azide (tosyl azide). Although this mode of preparation was followed for the majority of the reported experiments a new synthesis of 22 was also developed in the course of this study.

Oxidation of 2-propyn-1-ol (18) with chromium trioxide as described by Sauer ⁶³ afforded the acetylenic aldehyde (19) in low yield. Condensation of the acetylene with N-methylaniline gave a good yield of the enamine (20).⁶⁴

The co-reactant, tosyl azide, was readily prepared by the procedure of von Doering and DePuy ⁶⁵ from tosyl chloride and sodium azide.



Thus heating 20 with a 100% excess of tosyl azide at 70-80° under 0.2-5 mm pressure yielded a yellow oil in ca 50% yield.*

The infrared spectrum was consistent with 22 and showed absorptions at 2750 and 2830 cm^{-1} for the symmetric and asymmetric stretching frequencies of the CH aldehyde. A band at 3110 cm^{-1} was assigned to the stretching of the hydrogen attached to the carbon bearing the diazo group. A doublet at 2125 and 2100 cm^{-1} was consistent with the diazo function, and the 1640 cm^{-1} band was characteristic of the carbon-oxygen stretch of an α -diazocarbonyl compound.

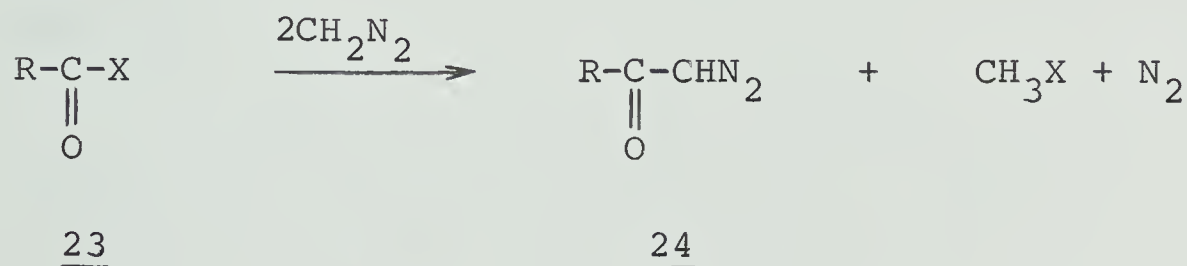
The diazoacetaldehyde was analysed by adding a solution of a weighed sample in THF to an excess of aqueous hydrochloric acid and measuring the nitrogen evolved. The

* Arnold reported ⁶² a 75% yield but did not quote the pressure or amount of excess tosyl azide employed.

purity was estimated to be generally in excess of 95%.

The preparation of diazoacetaldehyde by this procedure of Arnold was somewhat tedious and the overall yield from 2-propyn-1-ol was of the order of 7%. Thus a more convenient method of synthesis was sought.

The general method of preparation of an acyl substituted diazomethane (24) involves reaction of an acid chloride (23, X=Cl) or anhydride (23, simple X=OCOR, mixed X=OCOR') with two or more equivalents of diazomethane.



However, formyl chloride is unstable at normal temperatures, and formic anhydride is unknown. It was decided therefore to investigate the reaction of the formylating reagent formic acetic anhydride ⁶⁶ (23, R=H, X=OCHO) with diazomethane.

Addition of an ethereal solution of the anhydride to a diazomethane solution (1:5 molar ratio) at 0° resulted in the formation of diazoacetaldehyde. The product was isolated in 46% of good purity and the procedure constituted a fairly straightforward method for the preparation of 22, especially on a preparative scale.

A solution of 22 in THF was added to a solution of trihexylborane in the same solvent at 0-10°. Nitrogen evolution was smooth but only 40% of theory was obtained, although no diazo compound could be detected (ir). After hydrolysis with water the yield of n-octanal was determined as 22%.

The experiment was repeated. At room temperature 65% of theory (N₂) was evolved and a further 16% was achieved by refluxing the solution for one hour. However, on hydrolysis the yield of aldehyde was estimated to be only 3%.

A further experiment was undertaken using the less bulky boron compound, triethylborane. Nitrogen evolution at 25-30° was smooth and quantitative, but after hydrolysis the yield of n-butanal was observed to be negligible.

The addition of 2,4-dinitrophenylhydrazine (2,4DNP) reagent to a sample of the reaction mixture precipitated an orange solid. This material was shown to contain at least four components by tlc.

The conclusions drawn from these three experiments were that 22 was reacting to some extent with the boranes in the desired manner at ice-bath temperatures but reaction at ambient temperature and above was causing the product to react further. Some form of condensation of the aldehyde would seem to be indicated by the appearance of at least four components with 2,4-DNP reagent.

In an attempt to limit this further reaction, tri-butylborane and 22 were reacted at 0-10°. Nitrogen evolution was quantitative and an infrared spectrum prior to hydrolysis confirmed the absence of diazo and showed two weak and nearly equal intensity absorptions at 1730 and 1670 cm^{-1} .

The addition of water caused the lower frequency band to decrease with a concomitant increase in the intensity of the higher frequency absorption. This would indicate that the 1670 cm^{-1} band was due to a functionality in the intermediate, prior to hydrolysis.

After standing for 16 hours the yield of n-hexanal was estimated as 47% by quantitative infrared and as 44% by glc. This result was encouraging and seemed to confirm that a lower reaction temperature favored the formation (or stability) of the aldehyde.

The reaction of 22 with triethylborane was then repeated at 0-5°. Gas evolution was quantitative and the infrared spectrum of the reaction mixture again exhibited two bands at 1730 and 1675 cm^{-1} , in the ratio of ca 1:2.

The presence of the band at 1730 cm^{-1} indicated the presence of free aldehyde, prior to formal hydrolysis and this was confirmed by glc. The yield of n-butanal was estimated as 40%.

It was surprising therefore that the dropwise addition

of a slight molar excess of water at 0-5° caused the yield of aldehyde to decrease, until after 24 hours the yield had fallen to ca 17%.

Since the relatively slow addition of water had caused the aldehyde to react further it was decided to add an excess of water to the organoborane solution before the addition of 22, in the hope of "quenching" any further reaction.

Compound 22 was added to triethylborane, containing a 25 molar excess of water, at 0-5°. Nitrogen evolution was smooth initially but soon slowed and ceased at 79% of theory.

The yield of n-butanal was determined as 65% by glc, but significantly did not alter on standing.

The incomplete liberation of nitrogen from the diazo compound in the presence of water had been observed previously by Linke.⁶⁷ No explanation of this manifestation has as yet been uncovered. However, since the rate of reaction had been initially rapid, it was felt that complete nitrogen liberation could be accomplished by the addition of an excess of the borane.

When 22 was reacted with an arbitrary excess of triethylborane in THF containing water (molar ratio, 1:1.76:29.4) at 5-10°, nitrogen evolution was again quantitative and the yield of aldehyde had increased to

88% based on the diazo compound. A sample of n-butanal was isolated by preparative glc and the infrared and mass spectra of the isolated material were identical to those obtained from authentic aldehyde. Addition of 2,4-DNP reagent to an aliquot of the original reaction mixture precipitated the 2,4-DNP derivative; the yield (calculated from the weight of precipitate) was 86%.

The nmr spectra of the 2,4-DNP derivatives of the aldehyde products were found to be readily interpretable and proved of assistance in confirmation of structure. This technique eliminated the need for time-consuming isolation of sufficient pure aldehyde for nmr spectroscopy by preparative glc. In general only a few milligrams were isolated by this technique for infrared and mass spectroscopy.

The nmr spectra of these derivatives showed a broad singlet at ca τ - 1.08 due to the proton on nitrogen. A doublet at ca τ 0.88 with $J = 2.5$ Hz was due to the H-3 proton on the benzene ring. This proton experiences a large downfield shift due to the two adjacent nitro groups and shows the meta coupling to H-5. This latter proton, adjacent to one nitro group, appeared at ca τ 1.67 with ortho and meta couplings of 10 and 2.5 Hz, respectively. The third aromatic proton, H-6, showed as a doublet centered at ca τ 2.06 with $J = 10$ Hz, consistent with the ortho

coupling to H-5. The original aldehyde proton was shifted upfield and appeared as a triplet at ca τ 2.38. The α -methylene protons appeared at ca τ 7.59 (multiplet) and the remainder of the alkyl chain was observed at the normal positions expected for methine, methylene and methyl protons.

Thus a reasonable yield of n-butanal had been achieved from the borane derived from ethylene. It was decided therefore to screen a representative range of olefins to observe the effect of structure on the process. The results are summarised in Table II.

In the subsequent experiments the amount of water employed was reduced to an approximately 10-fold excess with no obvious deleterious effect.

From these results it is apparent that the more hindered organoboranes, with the possible exception of tricyclopentylborane, give the lowest yields of homologated product. This observation is in keeping with the results of previous workers.^{51,52}

Hydroboration of monosubstituted terminal olefins is known³⁶ to produce ca 94% primary and 6% secondary alkyl groups. In the reaction of the trialkylborane derived from butene-1 with 22 it was shown that the product derived from migration of the secondary alkyl group, 3-methylpentanal, was absent, or at the most, was formed in < 1% yield. This indicates that, in this reaction, the

TABLE II

Reaction of Trialkylboranes with Diazoacetaldehyde in
the Presence of Water.

| | Molar Ratios | | | | |
|-----------------------|--------------|--------------------|--------------------|-----------|--------------------|
| Olefin | <u>22</u> | : R ₃ B | : H ₂ O | T(°C) | Yield ^b |
| Ethylene ^a | 1 | : 1.76 | : 29.4 | 5-10 | 88 |
| Butene-1 | 1 | : 1.64 | : 10.9 | 5-10 | 77 |
| Butene-2 | 1 | : 1.52 | : 10.1 | 28-reflux | 33 |
| Isobutene | 1 | : 1.49 | : 9.9 | 28-40 | 67 |
| Cyclopentene | 1 | : 1.80 | : 12.0 | 26-30 | 98 |

^a Triethylborane was purchased from Callery Chemical Co.

^b Aldehyde by glc analysis.

secondary alkyl group migrates with less facility than the primary. Thus the aldehyde is formed free from isomeric impurity.

The reaction was extended to arylboranes by the conversion of triphenylborane to phenylacetaldehyde in 76% yield.

Attempts to isolate the aldehyde from the residual boron-containing material by distillation met with loss of product as had been noted by Brown.⁶⁸ Cyclopentylacetaldehyde was prepared from cyclopentene and reduced in situ with sodium borohydride. The formation of the alcohol meant that oxidative hydrolysis could be used to give cyclopentanol and water-soluble boron compounds. The residue after aqueous extraction was distilled to afford cyclopentanol and left 2-cyclopentylethanol as the residue in 72% yield.

In conclusion, the reaction of diazoacetaldehyde with organoboranes in the presence of water provides a novel route to aldehydes and further extends the utility of these versatile organometallic reagents.

Attempted Reaction of Two Boronic Acid Esters with
Ethyl Diazoacetate.

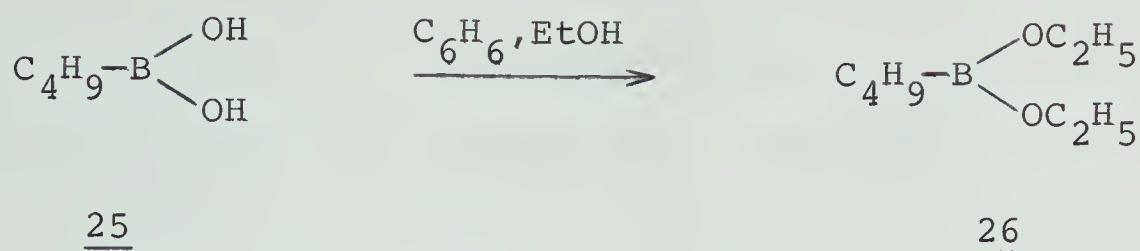
Attempts to react more than one alkyl group of a trialkylborane by using an excess of diazosubstrate have proven unsuccessful.⁶⁷ Therefore an inherent limitation of using trialkylboranes in organic synthesis is that the yield of product is necessarily maximised at 33.3% based on the olefin. With simple olefins this factor is acceptable, but the utility of these methods is seriously limited for more complex and less readily available alkenes.

Brown⁶⁹ has circumvented this difficulty by using 9-borabicyclo[3.3.1]nonane as the hydroborating agent.

A brief investigation to find an alternative procedure was initiated. A possible solution was sought in the use of an organoborane containing one alkyl group and two alkoxy groups, ie a boronic acid ester. Thereby only one equivalent of alkene is required and two equivalents of a readily available alcohol would provide the alkoxy groups.

n-Butylboronic acid (25) was available commercially (Callery Chemical Co.) and was readily converted to the diethyl ester (26) by the Fischer esterfication technique of Brindley et al.⁷⁰

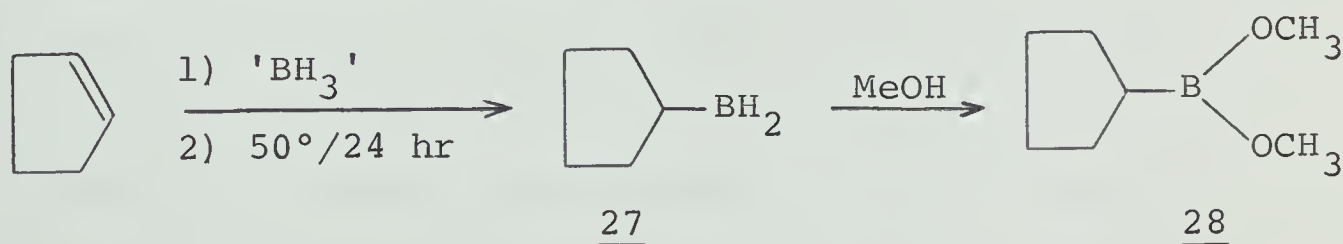
The ester was obtained as a colorless oil and the infrared spectrum was consistent with the formulation (26),



but no reported physical data could be found to confirm the structure.

A solution of 26 in THF was added to a solution of ethyl diazoacetate at less than 10° but no reaction was observed. After 3 hours at reflux 19% of theory (N₂) had been evolved. The absence of ethyl hexanoate after hydrolysis was confirmed by glc.

It was decided to try a second boronic ester, one which had been previously reported. Dimethyl cyclopentylboronate (28) was prepared by the method of Brown and Tsukamoto⁷¹ by hydroboration of one equivalent of cyclopentene, heating at ca 50° for 24 hours to cause equilibration of the organoboranes to form predominantly the monoalkyldihydro derivative (27), and then methanolysis of this intermediate to form the product 28.



The product obtained exhibited physical properties in good agreement with those reported⁷¹ and the infrared and nmr

spectra were also consistent with structure 28.

However, the attempted reaction of 28 with ethyl diazoacetate was unsuccessful. Nitrogen evolution was only 5% after a reflux period and the infrared spectrum of the mixture showed a negligible decrease in the concentration of ethyl diazoacetate.

It is felt that the lack of reactivity of these boronic acid esters, in marked contrast to their tri-alkyl borane analogs, may be explicable in terms of the decreased electrophilicity of the boron atom in the former compounds. This decrease is thought to be due to interaction of the oxygen lone-pairs with the vacant p orbital of the boron atom. This "back-coordination", has been used to explain the monomeric structure ⁷² and a number of other observations of alkoxyboranes. Thus p π -p π bonding is postulated by Werner and O'Brien ^{73,74} to explain the frequency of stretching of the B-O bond in the infrared.

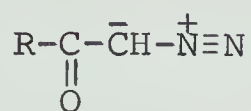
Lanthier ⁷⁵ has made a study of the boron-oxygen bonding in compounds such as $(\text{CH}_3)_2\text{BOCH}_3$ and $(\text{CH}_3)_2\text{BOB}(\text{CH}_3)_2$ by using the solvent dilution shifts in the nmr spectra to examine the Lewis-base character of the oxygen atom. He concluded that boron-oxygen π -bonding, rather than an inductive effect, is of predominant importance in determining the overall Lewis-acid character of these compounds. A barrier to rotation about the boron-oxygen bond of ca

9 kcals was also established by variable temperature nmr spectroscopy. This was considered to be a manifestation of the "back-bonding".

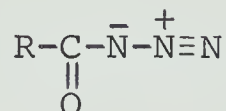
Therefore it would seem that the introduction of two alkoxy groups was sufficient to reduce the nucleophilicity of the borane to the extent that little or no complexation could occur with the diazo compound and no further work was undertaken.

Attempted Reaction of a Trialkylborane with an Azide

The reaction of trialkylboranes with diazoketones (29) has afforded an efficient synthesis of ketones.⁵¹ It was felt that a synthetic route to amides might be realised by reaction of trialkylboranes with acyl azides (30), compounds which are isoelectronic with the diazoketones.



29

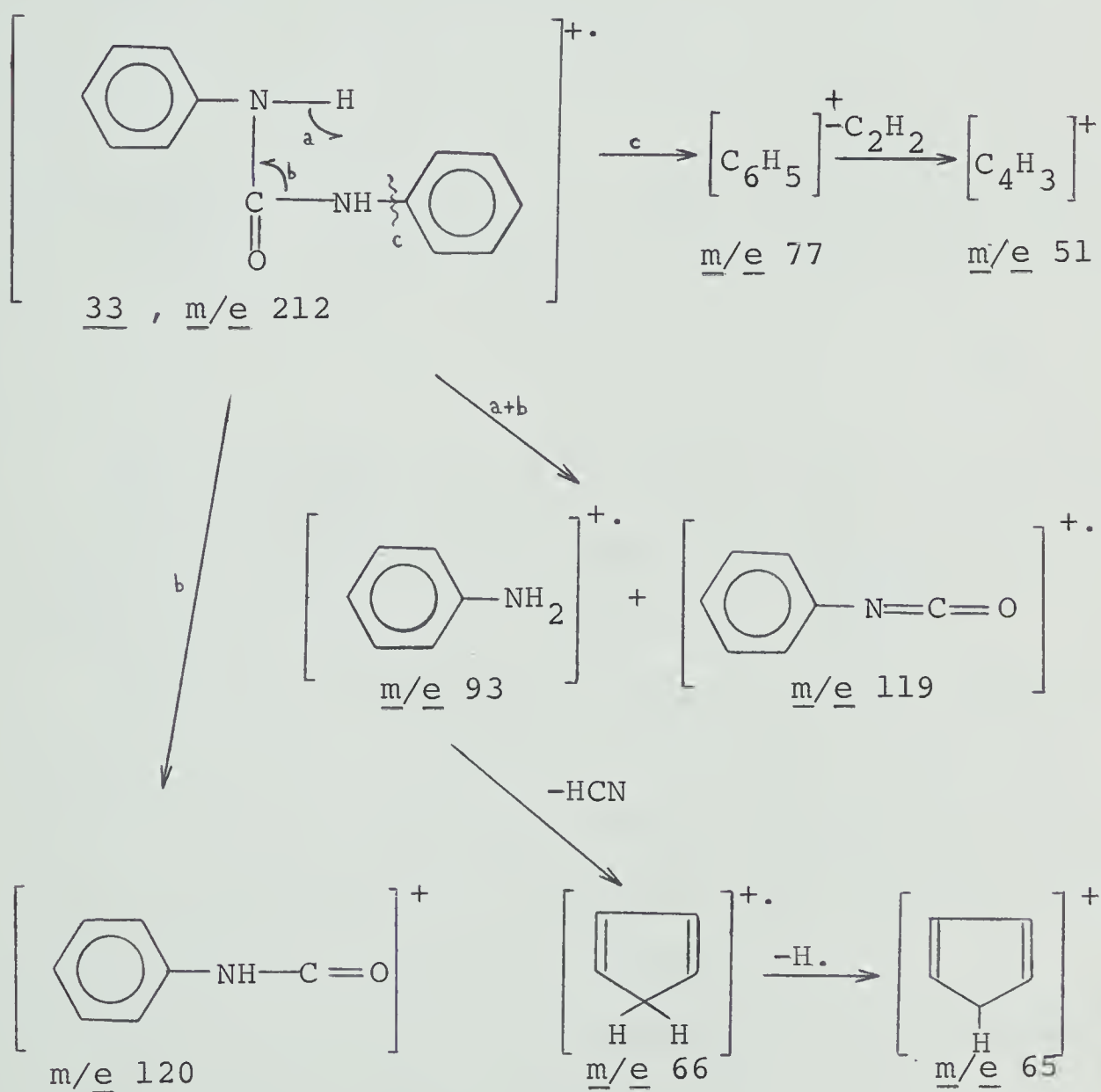


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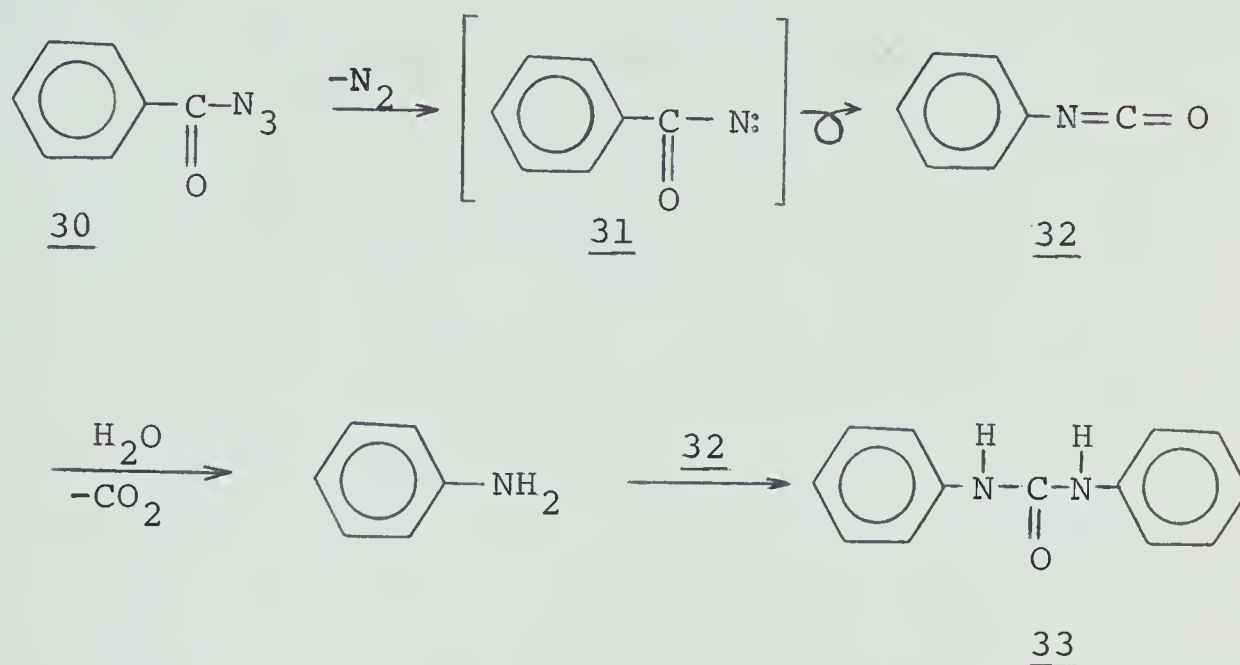
Benzazide (30, R = C₆H₅) was prepared by reaction of sodium azide and benzoyl chloride in aqueous acetone as described by Barrett and Porter.⁷⁶ A THF solution of the benzazide was added to tributylborane in THF at 5°. No reaction was apparent; the reaction was eventually refluxed for 7 hours to achieve quantitative nitrogen evolution. A white solid had precipitated and a small amount was removed prior to hydrolysis with water. *n*-Butylbenzamide, the expected product, was shown to be absent from the reaction mixture by glc but a significant precipitate of the white solid was present. This solid was filtered off and further crops were obtained by evaporation. The identity with the sample removed earlier was confirmed.

This material was identified spectroscopically as *N,N'*-diphenylurea (33). The infrared spectrum in Nujol showed a broad band at 3250 cm⁻¹ due to the NH stretching

and a strong band at 1645 cm^{-1} due to the urea carbonyl. Absorptions at 750 and 690 cm^{-1} confirmed the presence of a monosubstituted benzene. The mass spectrum showed a molecular ion at m/e 212, a base peak at m/e 93 and other major peaks at m/e 120, 119, 77, 66, 65 and 51. A rationale of these fragments is shown below.⁷⁷



The formation of this symmetrical urea in 57% yield may be explained in terms of a normal Curtius Reaction and probably does not involve the trialkylborane.



The hydrolysis of the isocyanate (32) may have been caused by traces of water added with the benzazide, which may not have been sufficiently dried.

Singleton and Edwards⁷⁸ heated 2-furoyl azide in diphenyl ether at 75-80° for two hours to obtain a 73% of 2-furyl isocyanate. These authors noted that sym-di-2-furylurea was formed whenever the isocyanate was exposed to moisture (atmospheric).

The reaction of trialkylboranes with acyl azides was not further investigated.

E X P E R I M E N T A L

Typical Preparation of Trialkylborane.³⁶ - A 100 ml 3-necked flask, fitted with a condenser, dropping funnel (sealed with a rubber septum), thermometer, magnetic stirring bar, gas inlet and outlet fittings and a rubber septum, was flame-dried while flushing with dry nitrogen. On cooling, anhydrous tetrahydrofuran (THF) (8 ml) was injected into the flask followed by a standardised⁷⁹ solution of borane in THF (Alfa Inorganics) (10 mmole). A solution of the olefin (30 mmole) in THF (8 ml) was added dropwise, keeping the temperature below 10° with an ice-bath. The mixture was finally stirred at room temperature for one hour to ensure complete hydroboration.

Diethyl Diazomalonate (7).⁵⁵ - Diethyl oxomalonate was prepared from diethyl malonate by the method of Dox,⁵³ and Corson and Hazen.⁵⁴ The colorless oil, bp 83-90°/5 mm (lit^{53,54} 81-86°/ 5 mm) was obtained in 47% yield. The hydrazone of diethyl oxomalonate was then prepared and oxidised with silver oxide as described by Ciganek⁵⁵ to give diethyl diazomalonate as a yellow oil, bp 92-94°/2 mm, $n_D^{24.5}$ 1.4641 (lit⁵⁵ 84-85°/1 mm, n_D^{24} 1.4650, n_D^{25} 1.4630), in 18% yield. Overall yield 9%.

ir (thin film) 2140 (N_2), 1758, 1736 (ester C=O), 1686 cm^{-1} (C=N).

Diethyl Diazomalonate (7).⁵⁶ - was prepared in 67% yield by treatment of diethyl malonate with *p*-toluenesulfonyl azide and diethylamine, as described by Rosenberger and Yates.⁵⁶ The product was obtained as a yellow oil, bp 73-75°/0.7 mm, n_D^{27} 1.4652 (lit ⁵⁵ 84-85°/1 mm, n_D^{25} 1.4630).

Reaction between Trihexylborane and Diethyl Diazomalonate. -

Trihexylborane (10 mmole) was prepared from hexene-1 (2.53g; 30 mmole), as outlined above. Diethyl diazomalonate (1.86g; 10 mmole) was added to this solution, while the closed system was connected to a gas burette (azotometer). The addition was completed at 30°, and after a further hour only 27% of the theoretical nitrogen (10 mmole) had been evolved. The reaction mixture was therefore refluxed for seven hours. On cooling to 30°, 81% (theory) nitrogen had been evolved. The mixture was cooled to 0-10° and 3N potassium hydroxide (10 ml) was added, followed by 30% hydrogen peroxide (5 ml). The mixture was stirred for 15 min at 0-10° and finally for one hour at 30°. Brine was added and the layers separated. The aqueous phase was extracted with THF (3 x 5 ml) and the washings and organic phase were combined and made up to 50 ml in a standard flask.

The infrared spectrum indicated approximately 21% unreacted diethyl diazomalonate, by comparison with authentic material.

Glc analysis (10% Carbowax 20M; 110°) indicated the presence of 1-hexanol, determined as 17 mmole/50 ml, and diethyl diazomalonate (24%). Diethyl n-hexylmalonate could not be detected (10% Carbowax 20M; 150°). All three were compared with standard solutions of authentic materials.

A chromatogram (10% Carbowax 20M; programmed 100° to 200° at 12°/min) showed a significant component at long retention time. This component was isolated by evaporation of a portion of the reaction solution, chromatography of the residue over Florisil using petroleum ether as eluant, and finally preparative glc (5% SE-30; 200°). The product was identified as the N-n-hexylhydrazone of diethyl oxomalonate. uv max (95% EtOH) 303 mμ ($\epsilon \sim 12,000$); ir (CCl₄) 3180 (hydrogen bonded NH), 2950 - 2850 (CH aliphatic), 1710 (ester C=O), 1650 (conjugated C=N), 1085 cm⁻¹ (ester); mass spectrum m/e 272 (Calcd for C₁₃H₂₄N₂O₄:272.1736. Found: 272.1737), 187, 141, 133, 115, 56, 55, 45, 44, 43, 42, 41, 32, 31, 29, 28 (base), 27.

The yield of the N-n-hexylhydrazone of diethyl oxomalonate was 22% by glc (5% SE-30:170°) using isolated material as standard.

Reaction between Trihexylborane and Diethyl Diazomalonate in Presence of Copper. - To a solution of trihexylborane

(10 mmole) in THF (prepared as described above) was added copper powder (electrolytic dust; 1g), followed by the slow addition of diethyl diazomalonate (1.86g; 10 mmole) in THF (8 ml). Since no reaction was observed at 10°, the temperature was raised to 28° and finally to reflux. After four hours at reflux only 18% (theory) nitrogen had been evolved.

The copper was filtered, and the filtrate hydrolysed (KOH-H₂O₂) as described in the preceding experiment. The product was made up to 100 ml in a standard flask.

Glc analysis (10% Carbowax 20M; 110°) revealed: 1-hexanol (10 mmole/100 ml); (10% Carbowax 20M; 150°C) diethyl diazomalonate (0%), diethyl n-hexylmalonate (0%), tetracarbethoxyethylene (0%); (5% SE-30; 170°) N-n-hexylhydrazone of diethyl oxomalonate (14%).

The aqueous hydrolysate was acidified and extracted with chloroform. No products were visible (glc).

Reaction between Trihexylborane and Diethyl Diazomalonate.

To a refluxing solution of trihexylborane (20 mmole) in THF (ca 30 ml) was added a solution of diethyl diazomalonate (3.72g; 20 mmole) in THF (30 ml) over a period of four hours. After a further two hours at reflux the nitrogen evolution was 12% (theory).

The reaction mixture was divided into three portions of (a) 20, (b) 20 and (c) 25 ml, which were treated as follows

- a) Hydrolysed ($\text{KOH-H}_2\text{O}_2$) as previously described). The organic layer and washings were made up to 50 ml in a standard flask.
- b) The second portion was hydrolysed with 3N potassium hydroxide (5 ml) at 10° and at 28° for one hour. The organic layer and washings were made up to 50 ml in a standard flask.
- c) The third portion was treated with water (1 ml) for one hour at 28° and the organic phase made up to 50 ml in a standard flask.

Diethyl n-hexylmalonate was shown to be absent in (a), (b) and (c) by glc. The yield of 1-hexanol was determined as: (a) 7 mmole/50 ml, (b) ca 1.7 mmole/50 ml, (c) ca 1.7 mmole/50 ml.

The yield of the N-n-hexylhydrazone of diethyl oxomalonate was estimated as: (a) 11%, (b) 20% and (c) 32%.

Reaction between n-Hexylmagnesium Bromide and Diethyl Diazomalonate. - A solution of n-hexylmagnesium bromide (5 mmole) in ether (10 ml) (prepared from 1-bromohexane (0.83g; 5 mmole) and magnesium turnings (5.4 mg atom)) was added to diethyl diazomalonate (0.93g; 5 mmole) in ether (10 ml). A sticky, yellow precipitate was formed immediately. The mixture was stirred for 0.5 hour, then hydrolysed by the addition of ammoniacal ammonium chloride

solution. The layers were separated and the aqueous phase extracted with ether (3 x 5 ml). The combined ethereal solutions were dried (sodium sulfate) and evaporated to yield a yellow oil. The product was shown to contain unreacted diethyl diazomalonate (ca 2 mmole), and a component having the same retention time as that of the N-n-hexylhydrazone of diethyl oxomalonate (10% Carbowax 20M; programmed 100° to 200° at 12°/min). The mixture was chromatographed over Florisil using petroleum ether as eluant. The N-n-hexylhydrazone of diethyl oxomalonate was further purified by preparative glc (15% Carbowax 20M; 160°).

uv max (95% EtOH) 303 mμ ($\epsilon = 14,300$); ir (CCl₄) 3150 (hydrogen bonded NH), 2940 - 2840 (CH aliphatic), 1710 (ester C=O), 1650 (conjugated C=N), 1080 cm⁻¹ (ester); mass spectrum m/e 272 (Calcd for C₁₃H₂₄N₂O₄: 272.1736. Found: 272.1737), 187 (base), 141, 115, 56, 45, 43, 41, 30, 29, 28, 27.

Propargyl Aldehyde (19).⁶³ - 2-Propyn-1-ol (112g; 2 mole) was oxidised with chromium trioxide in sulfuric acid, as described by Sauer,⁶³ to yield crude propargyl aldehyde (26g). The product was dried (MgSO₄) and distilled to a colorless, lachrymatory liquid, bp 51-54°/700 mm, in 17% yield.

ir (CHCl₃) 3290 (acetylene CH), 2850 and 2730

(aldehyde CH), 2090 ($\text{C}\equiv\text{C}$), 1680 cm^{-1} ($\text{C}=\text{O}$ of $\alpha\beta$ -unsaturated aldehyde).

β -N-Methylanilinoacrolein (20).⁶⁴ - A solution of propargyl aldehyde (18.6g; 0.345 mole) in absolute ethanol (100 ml) was cooled in an ice-bath. Freshly distilled N-methylaniline (38g; 0.355 mole) in ethanol (30 ml) was added dropwise. After stirring for one hour at 27°, no acetylenic absorption was observed in the infrared spectrum. The solution was evaporated and the residue distilled to afford a viscous, yellow oil (ca 50g), bp 147°/0.5 mm. Trituration of the distillate with petroleum ether: diethyl ether (1:1) and cooling caused crystallisation to occur. The solid was recrystallised twice (ether) to afford pale yellow crystals, mp 46-47° (lit ⁶⁴ 48-49°) in 79% yield.

nmr τ 0.72 (d,1, $J=8$ Hz), 2.49(d,1, $J=15$ Hz), 2.75(m,5), 4.58(dd,1, $J=15, 8$ Hz), 6.72(s,3).

p-Toluenesulfonyl Azide.⁶⁵ - A solution of sodium azide (70g; 1.08 mole) in water (200 ml) was added with swirling to a solution of freshly distilled p-toluenesulfonyl chloride (170g; 0.89 mole) in 95% ethanol (1 liter). The mixture was allowed to stand for one hour, then poured into water (4 liters). The organic phase was separated, washed with water (3 x 1 liter) and finally dried (Na_2SO_4). p-Toluenesulfonyl azide was obtained as

a colorless oil in 79% yield.

Typical Preparation of Diazoacetaldehyde (22).⁶² - β -N-Methylanilinoacrolein (4.8g; 30 mmole) and p-toluenesulfonyl azide (11.8g; 60 mmole) were placed in a 25 ml flask fitted with a short-path combined distillation head and condenser. The receiver was cooled with Dry-Ice, and the flask heated to 70-80°, initially under a pressure of 5 mm which was reduced slowly to 0.2 mm over a period of 1.5 hour. Diazoacetaldehyde was obtained as a yellow oil, bp ca 35°/5 mm (lit ⁶² ca 40°/10 mm) in 51% yield.

ir (CHCl₃) 3110 (CH diazo), 2830 and 2750 (CH aldehyde), 2125 and 2100 (N₂), 1640 cm⁻¹ (C=O of α -diazocarbonyl).

The product was analysed thus: A known weight of product (2-3 mmole) was dissolved in THF (3 ml) and added to 1N hydrochloric acid (20 ml). The nitrogen evolved was measured.

CAUTION: All operations were conducted behind safety shields.

Formic Acetic Anhydride (23).⁶⁶ - A solution of freshly distilled acetyl chloride (43g; 0.55 mole) in anhydrous ether (25 ml) was treated with sodium formate (46g; 0.68 mole) as described by Muramatsu et al.⁶⁶ The ether was evaporated under reduced pressure and the residue distilled

to give formic acetic anhydride as a colorless oil, bp 41-42°/30 mm (lit ⁸⁰ 36-38°/28 mm) in 78% yield.

ir (CCl₄) 1795 and 1777 cm⁻¹ (C=O of anhydride).

Diazoacetaldehyde (22). - Diazomethane (ca 0.8 mole) was prepared from N,N'-dimethyl-N,N'-dinitrosoterephthalamide (DuPont EXR101; 180g; 0.5 mole) by the procedure described in Organic Synthesis,⁸¹ and dried over potassium hydroxide pellets.

A solution of formic acetic anhydride (13.2g; 0.15 mole) in anhydrous ether (200 ml) was added to the diazomethane solution at 0° over a period of 2 hours.

After a further 2.5 hours at 0° the absence of anhydride was confirmed (ir) and the solvent and excess diazomethane was removed on the rotary evaporator using water pump pressure. Polymethylene was filtered off and the residue was distilled at reduced pressure, maintaining the bath temperature below 50°. ⁶² Diazoacetaldehyde was obtained as a yellow oil, bp 34-37°/8 mm (lit ⁶² ca 40°/10 mm) in 46% yield.

The ir spectrum was identical to that obtained for diazoacetaldehyde due to Arnold.⁶² The purity was estimated as 96% by azotometry.

CAUTION All operations were conducted behind safety shields.

Reaction between Trihexylborane and Diazoacetaldehyde -

Trihexylborane (10 mmole) was prepared as described above. Diazoacetaldehyde (0.44g; 6.3 mmole) in THF (8 ml) was added at 0-10°, and the system was connected to an azotometer. After stirring two hours (0-10°) and one hour at 24° ca 40% (theory) nitrogen had been evolved but absence of diazo compound was shown by ir. The mixture was hydrolysed by the addition of water (0.1 ml) and stirred overnight. The yield of n-octanal was estimated as 22%, using glc (15% Squalene; 120°) and comparison with a standard solution of authentic n-octanal.

Reaction between Trihexylborane and Diazoacetaldehyde -

Trihexylborane (10 mmole) was prepared as prescribed. Diazoacetaldehyde (0.45g; 6.4 mmole) in THF (8 ml) was added at 24°. About 65% (theory) nitrogen was evolved smoothly. The mixture was then refluxed for one hour and stirred overnight at 24°. Nitrogen evolution was estimated as 81% (theory). The yield of n-octanal was estimated to be 3% by glc (15% Squalene; 120°).

Reaction of Triethylborane with Diazoacetaldehyde - Tri-

ethylborane (Alfa Inorganics; 1.5 ml; ca 10 mmole) was added to THF (8 ml) under nitrogen. Diazoacetaldehyde (0.77g; 11 mmole) in THF (10 ml) was added slowly at 25-30°. Nitrogen evolution was 100% (theory). Water (1 ml) was added and the solution stirred for one hour at

28° before making up to 50 ml in a standard flask. The yield of n-butanal was estimated as < 4% by glc analysis (10% Squalane; 30°).

An aliquot of the reaction mixture was treated with 2,4-dinitrophenylhydrazine reagent and the resultant precipitate was shown (tlc) to contain at least four components none of which was coincident with the 2,4-DNP of authentic n-butanal.

Reaction between Tributylborane and Diazoacetaldehyde - Tributylborane (Callery Chemical Co; 2.5 ml; ca 9 mmole) was added to THF (10 ml) under nitrogen. Diazoacetaldehyde (0.42g; 6 mmole) in THF (10 ml) was added (one hour) at 0-10°. Nitrogen evolution was quantitative. An infrared spectrum of the reaction mixture showed two approximately equal, weak absorbances at 1730 and 1670 cm^{-1} respectively.

Water (0.18 ml; 10 mmoles) was added at 24°. After four hours the band at 1730 cm^{-1} in the infrared spectrum had increased approximately three-fold, while the 1670 cm^{-1} absorbance had decreased by a similar factor. The solution was stirred overnight and then made up to 50 ml in a standard flask. The yield of n-hexanal was determined as 44% by glc (10% Squalane; 70°).

The yield of n-hexanal was determined as 47% by

ir (1730 cm^{-1} absorption band). Both estimates were calculated by comparison with a standard solution of authentic material.

Reaction of Triethylborane and Diazoacetaldehyde - Diazoacetaldehyde (11 mmole) in THF (16 ml) was added slowly at 0.5° to a solution of triethylborane (Callery; 1.6 ml; ca 11 mmole) in THF (15 ml). Nitrogen evolution was smooth and quantitative:

An infrared spectrum of the colorless solution showed a broad band at 3390 cm^{-1} (bonded OH) and bands at 1730 and 1675 cm^{-1} (the absorbance of the latter band was about twice that for the 1730 cm^{-1} absorption). The yield of n-butanal was determined as 40% at this stage by glc.

Water (0.2 ml; 11 mmole) was added at $0-5^\circ$ to the stirred solution. An aliquot was removed after 15 min and the yield of n-butanal was estimated as 32% by glc (20% diethylene glycol succinate (DEGS); 90°).

The yield (glc) was 30, 28 and 28% in three successive estimations after a further 15, 20 and 25 min respectively.

After stirring the solution at 0° for 24 hours the yield of n-butanal had fallen to 17%.

Corresponding shifts in the intensity of absorbance of the band at 1730 cm^{-1} in the ir spectrum were noted.

Reaction between Triethylborane and Diazoacetaldehyde -

Water (4.5 ml; 250 mmole) was added to a solution of triethylborane (1.6 ml; ca 11 mmole) in THF (15 ml). Diazoacetaldehyde (ca 10 mmole) in THF (15 ml) was added slowly at 0-5°. Nitrogen evolution, initially smooth, became sluggish towards the end of the addition period and only 79% (theory) was evolved.

The band at 2100 cm^{-1} due to diazo compound was visible in the infrared spectrum of the yellow solution. The solution was treated with brine and the organic layer was separated, dried (MgSO_4) and made up to 50 ml in a standard flask.

The yield of n-butanal was estimated as 65% by glc (20% DEGS; 80°).

Reaction between Triethylborane and Diazoacetaldehyde -

Diazoacetaldehyde (8.5 mmole) in THF (10 ml) was added to a solution of triethylborane (ca 15 mmole) and water (4.5 ml; 250 mmole) in THF (15 ml) at 5-10°. Gas evolution was smooth and quantitative. The solution was filtered free from a small amount of solid material and made up to 50 ml in a standard flask. The yield of n-butanal was estimated as 88% by glc.

An aliquot of the reaction solution was distilled under nitrogen to remove solvent. n-Butanal was isolated from the residue by preparative glc (15% Squalene; 60°); ir (CCl_4) 2960 - 2870 (aliphatic CH), 2810 and 2710

(aldehyde CH), 1730 cm^{-1} (C=O); mass spectrum $\underline{m/e}$ 72 (corresponds to $\text{C}_4\text{H}_8\text{O}$), 57, 44, 43, 42, 41, 29 and 27.

An aliquot (2.5 ml) of the reaction mixture was added dropwise to 2,4-dinitrophenylhydrazine (2,4-DNP) reagent (0.1M in H_3PO_4) (10 ml). The precipitate was digested with 20 ml 2N hydrochloric acid for 3 hours, then filtered into a tared Gooch crucible, washed with water until chloride-free and dried in an oven (80°) and finally a vacuum desiccator. The precipitate (0.1026g) mp 108° (lit ⁸² 122°), was shown to contain ca 10% 2,4-dinitrophenylhydrazine by nmr. Thus the yield of n-butyraldehyde was 86% by this gravimetric technique.

nmr τ - 1.08 (broad s,1), 0.87(d,1, $J=2.5\text{ Hz}$), 1.67(d of d,1, $J=10, 2.5\text{ Hz}$), 2.06(d,1, $J=10\text{ Hz}$), 2.37 (t,1, $J=5\text{ Hz}$), 7.58(m,2), 8.31(m,2), 8.96(m,3); also superimposed signal τ 7.86 (d) due to free hydrazine; mass spectrum $\underline{m/e}$ 252 (corresponds to $\text{C}_{10}\text{H}_{12}\text{N}_4\text{O}_4$), 238, 152, 122, 79, 78, 77, 75, 63, 55, 51, 43, 41, 30, 28, 27.

Reaction between Tributylborane and Diazoacetaldehyde -

Tributylborane (15 mmole) was prepared as prescribed from butene-1. Water (1.8 ml; 100 mmole) was added, followed by diazoacetaldehyde (9.1 mmole) in THF (10 ml) at $0-10^\circ$. Gas evolution was smooth and quantitative. The colorless solution was made up to 50 ml in a standard flask.

The yield of n-hexanal was determined as 77% by glc (10% Squalane; 90°) and as 71% by quantitative preparation of the 2,4DNP derivative. 3-Methylpentanal was shown to be absent (glc).

n-Hexanal was isolated by preparative glc (15% Squalene; 115°) from a concentrated sample of the reaction mixture.

ir (CCl_4) 2950 - 2860 (aliphatic CH), 2810 and 2710 (aldehyde CH), 1730 cm^{-1} (C=O); nmr τ 0.22(t,1, J=2 Hz), 7.59(m,2), ca 8.5(m,4), 9.11(m,3); mass spectrum m/e 100 (corresponds to $\text{C}_6\text{H}_{12}\text{O}$), 82, 72, 71, 57, 56, 44, 43, 41.

The 2,4-DNP was also prepared from this isolated sample, and was obtained as yellow crystals, mp 103° (lit ⁸² 104°).

nmr τ -1.07(broad s,1), 0.89(d,1, J=2.5 Hz), 1.67 (d of d, 1, J=10, 2.5 Hz), 2.06(d,1, J=10 Hz), 2.38(t,1, J=5 Hz), 7.58(m,2), 8.55(m,6), 9.08(m,3).

Reaction between Triisobutylborane and Diazoacetaldehyde - Triisobutylborane (15 mmole) was prepared from isobutene as prescribed. Water (1.8 ml; 100 mmole) was added, followed by diazoacetaldehyde (10 mmole) in THF (10 ml) at 25°. Nitrogen evolution was sluggish. The reaction temperature was raised to 40°; gas evolution was essentially quantitative. The reaction mixture was diluted to 50 ml in a standard flask.

The yield of 4-methylpentanal was estimated as 67% by glc (10% Squalane; 45°) and 73% by quantitative 2,4-DNP.

The aldehyde was isolated by preparative glc (20% NPGSE; 70°) as a colorless liquid; ir (CCl_4) 2950 - 2850 (aliphatic CH), 2800 and 2700 (aldehyde CH), 1730 cm^{-1} (C=O).

The 2,4-DNP derivative was recrystallised (95% EtOH) to give golden-yellow crystals, mp 96-98° (lit ⁸³ 99°).

nmr τ - 1.05(broad s,1), 0.93(d,1, J=2.5 Hz), 1.66 (d of d, 1, J=10, 2.5 Hz), 2.06(d,1, J=10 Hz), 2.41 (t, 1, J=5 Hz), 7.58 - 8.43(m,5), 9.04(d,6, J=5 Hz).

Reaction between Tri-2-butylborane and Diazoacetaldehyde -
Tri-2-butylborane (15 mmole) was prepared from butene-2. Water (1.8 ml; 100 mmole) was added, followed by diazoacetaldehyde (9.9 mmole) in THF (10 ml). The temperature was gradually raised to about 45° and finally to reflux to ensure liberation of nitrogen, which was nearly quantitative. The deeply colored solution was made up to 50 ml in a standard flask.

The yield of 3-methylpentanal was estimated as 33% by glc (10% Squalane; 55°).

An aliquot of the reaction mixture was added to 2,4-DNP reagent and the precipitate was filtered off and chromatographed over Florisil using benzene as eluant using tlc to monitor the fractions. The homogeneous

fractions were combined and the product was recrystallised (95% EtOH) to afford golden-yellow crystals, mp 94-95° (lit ⁸³ 93.5-94.5°); nmr τ - 1.13(broad s,1), 0.84 (d,1, J=2.5 Hz), 1.64(d of d,1, J=10, 2.5 Hz), 2.03(d,1, J=10 Hz), 2.37(t,1, J=5 Hz), 7.60(m,2), ca 8.4(m,3), 8.88 (m,3), 8.99(m,3).

Reaction between Tricyclopentylborane and Diazoacetaldehyde.-

Tricyclopentylborane (15 mmole) was prepared from cyclopentene. Water (1.8 ml; 100 mmole) was added, followed by a solution of diazoacetaldehyde (8.4 mmole) in THF (10 ml) at 25-30°. Nitrogen evolution was smooth and quantitative. The solution was diluted to 50 ml.

The yield of cyclopentylacetaldehyde was estimated as 98% by glc (10% Squalane; 100°) and as 90% by quantitative 2,4-DNP precipitation.

A sample of the reaction mixture was treated with brine and extracted with pentane. The organic layer was separated, washed with water, dried (Na₂SO₄) and evaporated. Cyclopentylacetaldehyde was isolated from the residue by preparative glc (15% Squalene; 130°C) as a colorless liquid; ir (CCl₄) 2950-2870 (aliphatic CH), 2715 (aldehyde CH), 1730 cm⁻¹ (C=O); mass spectrum m/e 112 (corresponds to C₇H₁₂O), 68, 55, 41.

The 2,4-DNP derivative was recrystallised (95% EtOH) to afford golden-yellow crystals, mp 126-128° (lit ⁸⁴ 128-129°); nmr τ - 1.03(broad s,1), 0.90(d,1, J=2.5 Hz), 1.69

(d of d, 1, $J=10$, 2.5 Hz), 2.09(d, 1, $J=10$ Hz), 2.42(t, 1, $J=5$ Hz), 7.60(m, 3), centred ca 8.3(m, 8); mass spectrum m/e 292 (corresponds to $C_{13}H_{16}N_4O_4$), 224, 206, 149, 95, 69, 67, 55, 41.

Analysis: Calcd for $C_{13}H_{16}N_4O_4$: C, 53.42; H, 5.52; N, 19.17. Found: C, 53.41; H, 5.51; N, 18.90.

Reaction between Triphenylborane and Diazoacetaldehyde -

Triphenylborane (Aldrich Chemical Co., 3.63g; 15 mmole) was dissolved in THF (30 ml). Water (1.8 ml; 100 mmole) was added and then a solution of diazoacetaldehyde (10.6 mmole) in THF (10 ml) was added dropwise at 0-10°. The temperature was raised to 20-30°. Gas evolution was 90% (theory), and the reaction mixture was made up to 50 ml in a standard flask. The yield of phenylacetaldehyde was estimated as 76% by glc (15% Apiezon L; 160°).

A sample of the reaction mixture was treated with brine and extracted with pentane. The organic layer was separated and treated with a fresh portion of brine (5 x 10 ml). Each addition was observed to cause precipitation of a white solid. Finally the organic phase was dried (Na_2SO_4) and evaporated.

Phenylacetaldehyde was isolated from the residue by preparative glc (15% Apiezon L; 160°) as a colorless oil, ir (CCl_4) 3070-3020 (aromatic CH), 2900 (aliphatic CH), 2805 and 2710 (aldehyde CH), 1730 cm^{-1} (C=O).

An aliquot (5 ml) of the reaction mixture was added to 2,4-DNP reagent as described previously. However, only an orange oil was formed. The aqueous mixture was extracted with chloroform and the organic layer was concentrated and chromatographed over neutral (Woelm) alumina using carbon tetrachloride:benzene (1:1 by volume) as eluant. Yellow-orange crystals were obtained.

nmr τ - 1.08 (broad s,1), 0.89(d,1, J=2.5 Hz), 1.65 (d of d,1, J=10, 2.5 Hz), 2.03(d,1, J=10 Hz), 2.38(t,1, J=5 Hz), 2.68(m,5), 6.25(d,2, J=5 Hz).

2-Cyclopentylethanol - Tricyclopentylborane (30 mmole) was reacted with diazoacetaldehyde (17.6 mmoles) as described above. However on completion of the gas evolution the reaction mixture was treated with aqueous sodium borohydride at 25°. After one hour the mixture was cooled in an ice-bath and 3N sodium hydroxide (20 ml) and 30% hydrogen peroxide (10 ml) were added, keeping the temperature below 10°. Brine was added and the layers were separated. The aqueous phase was extracted with pentane (3 x 50 ml) and the combined organic phase and washings were washed with brine (1 x 80 ml), water (3 x 50 ml), dried (Na_2SO_4) and evaporated. The residue was distilled to afford cyclopentanol and left the 2-cyclopentylethanol (1.55g), n_D^{25} 1.4612 (lit n_D^{19} 1.4572) as the residue. The product was estimated to be 94% pure by glc, with ca 4% cyclopentanol as the major impurity.

ir (CCl_4) 3595 (free OH), 3320 (bonded OH), 2920-2840 (aliphatic CH), 1085 cm^{-1} (primary OH); nmr τ 6.39(t,2, $J=6.5\text{ Hz}$), 7.61(s,1), ca 8.4(m,11).

Diethyl *n*-Butylboronate ⁷⁰ - *n*-Butylboronic acid (10.2g; 0.1 mole) was dissolved in a mixture of absolute ethanol (27.6g; 0.6 mole) and benzene (62.4g; 0.8 mole). The mixture was distilled using a Nester-Faust spinning-band column (60 cm x 1 cm). The ternary azeotrope was removed, bp $62^\circ/700\text{ mm}$, followed successively by the binary azeotrope, bp $65^\circ/700\text{ mm}$ and excess benzene.

The residue was distilled through a 10 cm Vigreux column to afford a colorless oil, bp $46-49^\circ/10\text{ mm}$ in 15% yield; ir (CCl_4) 2960-2855 (aliphatic CH), 1323 (B-O) ⁷³, 1048 cm^{-1} (C-O).

Attempted Reaction between Diethyl *n*-Butylboronate and Ethyl Diazoacetate. - Diethyl *n*-butylboronate (1.59g; 10 mmole) was dissolved in THF (10 ml). Ethyl diazoacetate (1.14g; 10 mmole) in THF (10 ml) was added slowly at $0-10^\circ$; when the absence of any reaction became apparent the reaction mixture was heated to reflux. After three hours at reflux only 19% (theory) nitrogen had been evolved.

The unreacted ethyl diazoacetate was estimated as 73% by comparison of the infrared spectrum with that of a standard solution.

The absence of ethyl hexanoate from a hydrolysed sample of the reaction mixture was confirmed by glc.

Dimethyl Cyclopentylboronate⁷¹ - was prepared as described by Brown and Tsukamoto.⁷¹ The ester was obtained as a colorless oil, bp 61-63°/20 mm, n_D^{21} 1.4310 (lit⁷¹ 60-62°/20 mm, n_D^{20} 1.4300) in 28% yield; ir (CCl₄) 2960-2870 (aliphatic CH), 1340 (B-O)⁷³, 1028 cm⁻¹ (C-O); nmr (CCl₄) τ 6.51(s,6), ca 8.5 (broad m,9).

Attempted Reaction between Dimethyl Cyclopentylboronate and Ethyl Diazoacetate - Ethyl diazoacetate (1.14g; 10 mmole) in THF (10 ml) was added to a solution of dimethyl cyclopentylboronate (1.42g; 10 mmole) in THF (25 ml) at 27°. The temperature was raised to 65° when it became apparent that the reaction was very slow. After three hours at 65° only 5% (theory) nitrogen had been evolved.

A comparison of the absorption band at 2100 cm⁻¹ in the infrared spectrum of the reaction mixture and a standard solution showed that practically none of the ethyl diazoacetate had reacted.

Benzazide⁷⁶ - An ice-cold solution of benzoyl chloride (17.5g; 0.125 mole) in acetone (40 ml) was added to an ice-cold solution of sodium azide (9.0g; 0.138 mole) in water (25 ml). The mixture was shaken occasionally while it was maintained at 0° for 30 min. The upper layer was then separated and dropped onto crushed ice. The resultant precipitate was filtered off, washed with

ice-cold water and dried in a vacuum desiccator to give white crystals, mp 27° (lit ⁷⁶ 32°) in 97% yield; ir (CCl_4) 2170 and 2130 (N_2), 1700 cm^{-1} (C=O).

Attempted Reaction between Tributylborane and Benzazide -

A solution of benzazide (2.83g; 19.2 mmole) in THF (20 ml) was added slowly to a solution of tributylborane (Callery Chemical Co.) (20 mmole) in THF (15 ml) at 5° . When no reaction was apparent the temperature was progressively raised until the mixture was refluxing. After seven hours at reflux the nitrogen evolution was quantitative.

On cooling, a white solid precipitated. A sample of the solid was removed and water (0.4 ml) was added at $0-10^{\circ}$ to the stirred mixture. After 15 min the solid was filtered, and the filtrate shown to be free of N-n-butylbenzamide (glc). The filtrate was evaporated and cooled to yield a further crop of crystals, which were again removed. The three samples were shown to be identical (ir) and the combined solid (1.16g) was recrystallised (95% EtOH) to afford white crystals, mp $241-243^{\circ}$ (lit ⁸⁶ N,N'-diphenylurea 242°); ir (Nujol) 3250 (broad, NH), 1645 (C=O urea), 750 and 690 cm^{-1} (C_6H_5); mass spectrum $\underline{m/e}$ 212 (corresponds to $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}$), 120, 119, 93 (base), 77, 66, 65 and 51.

Analysis: Calcd for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}$: C, 73.56; H, 5.70; N, 13.20. Found: C, 73.27; H, 5.74; N, 13.49.

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